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Radiochemistry of Manganese

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Revised Edition

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Subcommittee on Radiochemistry
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Foreword

The Subcommittee on Radiochemistry is one of a number of subcommittees working under the Committee on Nuclear Science within the National Academy of Sciences—National Research Council. Its members represent government, industrial, and university laboratories in the areas of nuclear chemistry and analytical chemistry.

The Subcommittee has concerned itself with those areas of nuclear science which involve the chemist, such as the collection and distribution of radiochemical procedures, the radiochemical purity of reagents, the place of radiochemistry in college and university programs, and radiochemistry in environmental science.

This series of monographs has grown out of the need for compilations of radiochemical information, procedures, and techniques. The Subcommittee has endeavored to present a series that will be of maximum use to the working scientist. Each monograph presents pertinent information required for radiochemical work with an individual element or with a specialized technique.

Experts in the particular radiochemical technique have written the monographs. The Atomic Energy Commission has sponsored the printing of the series.

The Subcommittee is confident these publications will be useful not only to radiochemists but also to research workers in other fields such as physics, biochemistry, or medicine who wish to use radiochemical techniques to solve specific problems.

Gregory R. Choppin, *Chairman*
Subcommittee on Radiochemistry

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Radiochemistry of Manganese

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revised from the original text of G. W. LEDDICOTTE

I. GENERAL REVIEWS OF THE CHEMISTRY OF MANGANESE.

A. Inorganic Chemistry

1. J. W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. XII, Longmans, London (1932), p 139-464.
2. N. V. Sidgwick, The Chemical Elements and Their Compounds, Vol. II, Oxford Univ. Press, London (1950), p 1264-1288.
3. A. H. Sully, Manganese, Academic Press, New York (1955).

B. Analytical Chemistry

1. M. D. Cooper and P. K. Winter in Treatise on Analytical Chemistry, I. M. Kolthoff and P. J. Elving editors, Part II, Vol. 7, Interscience Publishers, New York (1961), p 425-502.
2. E. B. Sandell, Colorimetric Determination of Traces of Metals, 3rd Ed., Interscience Publishers Inc., New York (1959).
3. N. H. Furman, editor, Standard Methods of Chemical Analysis, 6th Ed., Vol. I, D. Van Nostrand Co., Inc., New York (1962), p 638-655.
4. G. H. Morrison and H. Freiser, Solvent Extraction in Analytical Chemistry, John Wiley and Sons, Inc., New York (1957), p 217.
5. W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffman, Applied Inorganic Analysis, John Wiley and Sons, Inc., New York, (1953), p 439-451.
6. C. J. Rodden, editor, Analytical Chemistry of the Manhattan Project, McGraw Hill, New York (1950).

C. Radiochemistry

1. G. W. Leddicotte, "The Radiochemistry of Manganese", National Academy of Sciences - National Research Council Report NAS-NS-3018, Washington, D. C., (1960).
2. A. C. Wahl and N. A. Bornser, Radioactivity Applied to Chemistry, John Wiley and Sons, Inc., New York (1958).

II NUCLEAR PROPERTIES OF MANGANESE ISOTOPIES

Natural manganese consists of one stable isotope, ^{55}Mn , atomic number 25. This isotope is in the region of maximum nuclear stability; its binding energy is 8.76 MeV per nucleon and its atomic weight is 54.938054⁽¹⁾ based on $^{12}\text{C} = 12.000000$. The nuclear spin of ^{55}Mn is $5/2^-$. Very small but detectable amounts of radioactive ^{53}Mn and ^{54}Mn , produced by cosmic ray induced spallation reactions, are found in meteorites⁽²⁾. The relative abundances of these radioactive manganese isotopes have been used to determine both the age of meteorites and the time since they fell to earth. The determination of these isotopes is a challenging radiochemical problem⁽³⁾.

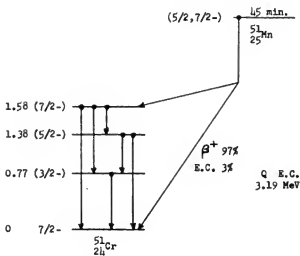
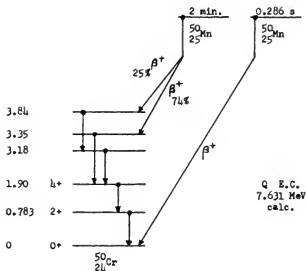
Manganese isotopes from mass number 50 to 58 have been produced; their properties and methods of production are summarized in Table II.1⁽⁴⁾. The decay schemes of these manganese isotopes, as given in the Table of Isotopes⁽⁴⁾, are given in Figure II.1. The most useful isotope for tracer studies is the 303 day ^{54}Mn which decays by electron capture and emits a 100% abundant 835 keV gamma ray. The major isotope of interest in activation analysis and flux monitoring is 2.576 hour ^{56}Mn which decays by beta emission and emits abundant 847, 1811, and 2110 keV gamma rays. The half life and characteristic gamma rays make ^{56}Mn an ideal isotope for activation analysis. Because ^{53}Mn decays solely by electron capture (emitting only Cr X-rays) and has a very long half life, it is extremely difficult to count and can be more accurately determined by activation to ^{54}Mn ⁽⁵⁾.

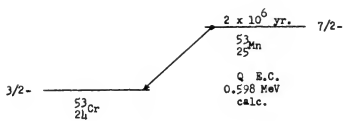
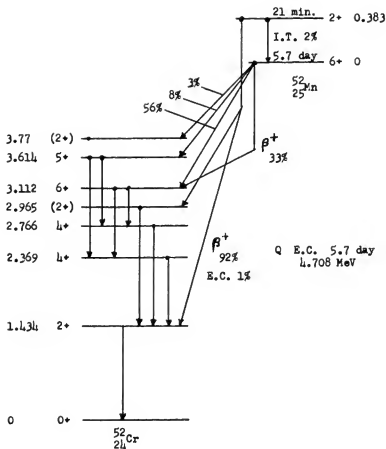
Neutron capture cross sections have been measured as a function of neutron energy for ^{55}Mn ⁽⁶⁾. The thermal (0.025 eV) cross section of ^{55}Mn is 13.3 barns and the resonance integral is 14.2 barns⁽⁷⁾. A capture cross section of 170 barns has been determined for ^{53}Mn ⁽⁸⁾ using typical reactor neutrons. Fast neutrons will produce 303 day ^{54}Mn by an $n,2n$ reaction on ^{55}Mn , and the reaction can be used for low sensitivity activation analysis or as a fast neutron flux monitor if the sample is free of iron. Other threshold reactions, n,p giving 3.5 min. ^{55}Cr , and n,α giving 3.8 min. ^{52}V , are possible with fast

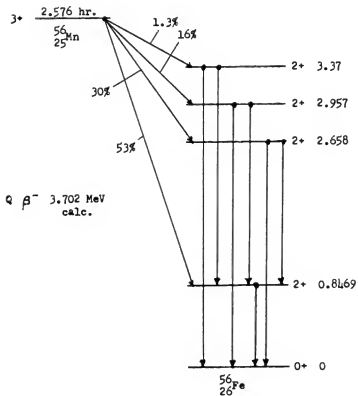
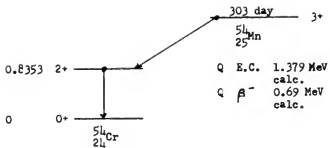
TABLE II.1
ISOTOPES OF MANGANESE⁽⁴⁾

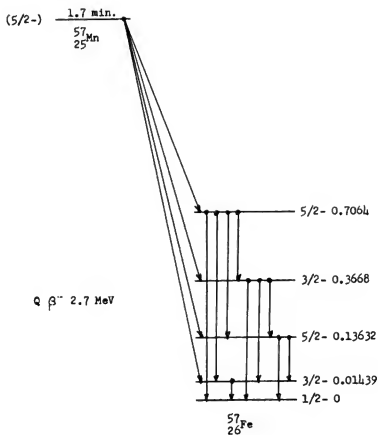
NUCLIDE	HALF-LIFE	TYPE OF DECAY		GAMMA RAYS		HOW MADE	NOTES
		Mode	Energy MeV	Energy MeV	Abundance %		
⁴⁹ Mn	0.4 sec.						uncertain
⁵⁰ Mn	0.286 sec.	β^+	6.61 max.	0.511 γ^+	200%	⁵⁰ Cr(p,n)	probable
⁵⁰ Mn	2 min.	β^+		0.511 γ^+	198%	⁵⁰ Cr(p,n)	uncertain
				0.66	25		
				0.783	100		
				1.11	100		
				1.28	25		
				1.45	75		
⁵¹ Mn	45.2 min.	β^+	2.17 max.	0.511 γ^+	194%	⁵⁰ Cr(d,n) ⁵⁰ Cr(p, γ)	certain
				1.56			
				2.03			
⁵² Mn	5.60 day	β^+ (34%) E.C. (66%)	0.575 max.	0.511 γ^+	67%	⁵² Cr(p, α) ⁵² Cr(d,2n)	certain
				0.744	82		
				0.935	84		
				1.434	100		
^{52m} Mn	21.1 min.	β^+ I.T. (2%)	1.63 max.	0.383	2%	⁵² Fe decay	certain
				0.511 γ^+	193		
				1.434	100		
⁵³ Mn	1.9x10 ⁶ yr.	E.C.		Cr X-rays		⁵³ Cr(p,n) ⁵² Cr(d,n)	probable
⁵⁴ Mn	303 day	E.C.		Cr X-rays		⁵⁶ Fe(d,x) ⁵⁴ Fe(n,p)	certain
				0.835	100%		
⁵⁵ Mn	stable	100% abundant					
⁵⁶ Mn	2.576 hr.	β^-	2.85 max.	0.847	99%	⁵⁵ Mn(n, γ) ⁵⁶ Fe(n,p)	certain
				1.811	29		
				2.110	15		
⁵⁷ Mn	1.7 min.	β^-	2.55 max.	Fe X-rays		⁵⁴ Cr(α ,p) ⁵⁷ Fe(n,p)	probable
				0.014	conv.		
				0.122	strong		
				0.136	strong		
				0.22			
				0.353			
				0.692			
⁵⁸ Mn	1.1 min.	β^-		0.36, 0.41		⁵⁸ Fe(n,p)	probable
				0.52, 0.57			
				0.82, 1.0			
				1.25, 1.4			
				1.6, 2.2			
				2.8			

FIGURE II.1
Decay Schemes of Manganese Isotopes⁽⁴⁾









neutrons. Charged particle and photonuclear reactions, $^{55}\text{Mn}(p,n)^{55}\text{Fe}$ (2.6 yr.), $^{55}\text{Mn}(p,pn)^{54}\text{Mn}$ (303 d.), $^{55}\text{Mn}(d,p)^{56}\text{Mn}$ (2,576 hr.), and $^{55}\text{Mn}(\nu,n)^{54}\text{Mn}$ (303 d.), are also of possible interest for activation analysis and producing tracers⁽⁹⁾.

Manganese can be determined with great sensitivity and very easily by thermal neutron activation analysis⁽⁹⁾. With reactors as the source of neutrons, the sensitivity of the analysis is of the order of 10^{-12} grams. The relatively high cross section of ^{55}Mn , coupled with the ideal half life and gamma spectrum of the ^{56}Mn capture product combine to make activation analysis particularly attractive. A large amount of the radiochemical work on manganese has been in conjunction with activation analysis. With the development of high resolution lithium drifted germanium gamma spectrometers, manganese can be determined by activation analysis with either no chemical separation or a simple group separation⁽¹⁰⁾. If highly thermalized neutrons are used, there is no interference in the analysis, but if typical reactor or radioactive source neutrons are used, iron will cause a serious interference due to the $^{56}\text{Fe}(n,p)^{56}\text{Mn}$ reaction; cobalt can also interfere due to the $^{59}\text{Co}(n,\alpha)^{56}\text{Mn}$ reaction. By irradiating samples both in highly moderated and hard neutron fluxes, the interferences due to iron and cobalt can be determined and corrections made⁽¹¹⁾. If the neutron irradiation is carried over a long time, manganese activity can be produced from chromium by the reaction sequence $^{54}\text{Cr}(n,\nu)^{55}\text{Cr}(\beta^-)^{55}\text{Mn}(n,\nu)^{56}\text{Mn}$. Various portable neutron sources have been used for manganese activation analysis; ^{252}Cf is a particularly attractive source⁽¹²⁾. Fast, 14 MeV, neutrons have also been used⁽¹³⁾.

A number of chemical separation procedures used in activation analysis are given in section VI. Because of the increased use of high resolution Ge(Li) gamma spectrometers in activation analysis, the interest in manganese radiochemical separations is decreasing. Activation analysis of manganese is extensively used in archeology⁽¹⁴⁾, agriculture⁽¹⁵⁾, geology⁽¹⁶⁾, and other fields⁽¹⁷⁾, and is especially valuable when the samples must not be destroyed.

Manganese has been extensively used as a neutron flux monitor. The reaction, $^{55}\text{Mn}(n,\gamma)^{56}\text{Mn}$, has been used as a neutron flux monitor from almost the time of discovery of the neutron. For short irradiations, small samples of a dilute alloy of Mn in Al are particularly useful flux monitors since they minimize the radiation dose upon discharge from the reactor and because of the small amount of manganese there is no self shielding of neutrons. Since 2.576 hour ^{56}Mn decays to stable ^{56}Fe , and since neutron capture in ^{56}Fe and ^{57}Fe both lead to stable iron isotopes, manganese can be used as a total integral neutron flux monitor for very long irradiations in high fluxes; the total integral flux being determined by the fraction of manganese converted to iron as determined by colorimetric analysis for iron and manganese^(7b).

A large bath of MnSO_4 solution is commonly used to obtain the absolute intensity of a neutron beam or source⁽¹⁶⁾. The hydrogen in the solution moderates the neutrons which are then largely captured by ^{55}Mn . A very sensitive neutron monitor for weak sources and beams is a bath of KMnO_4 solution. The ^{56}Mn neutron capture product is concentrated by a Szilard Chalmers reaction in the MnO_2 produced by the decomposition of the KMnO_4^- , and so, by filtering the irradiated solution, most of the activity can be concentrated on a small filter and so counted with high sensitivity⁽¹⁹⁾.

III REVIEW OF THE CHEMISTRY OF MANGANESE

1. Introduction

Manganese compounds have been known since prehistoric times. From the beginning, the glass industry has used manganese dioxide to remove the green tint in glass due to ferrous silicates, and in larger amounts as a color producer. Manganese metal was first produced by J. G. Gahn in 1774 by the reduction of manganese oxide by oil and charcoal⁽²⁰⁾. Manganese today is used extensively in industry, especially as an alloying and deoxidizing agent for steel.

2. Occurrence in Nature

Manganese is the eleventh most abundant element in the earth's crust,

being more abundant than such common elements as sulfur, copper, carbon, and zinc. It comprises about 0.1% of the lithosphere⁽²¹⁾. Manganese is present to the extent of about one part per million in average river water and about one to ten parts per billion in ocean water⁽²²⁾. The manganese brought into the ocean is slowly and nearly completely precipitated; the manganese nodules in the ocean being formed in this manner. Manganese is an essential (usually at the trace level) constituent of living tissue, both plant and animal. Its abundance varies from a few parts per billion to over one per cent; it is usually more abundant in plant than animal tissue. Manganese deficiency is a cause of disease in plants. Activation analysis has been an important tool in the determination of manganese in biological materials.

Manganese is one of the more abundant elements in meteorites where it has a somewhat greater abundance than in the earth's crust. Meteorites also contain detectable amounts of ^{53}Mn and ^{54}Mn formed by cosmic ray bombardment, see section II⁽²³⁾. Manganese is quite abundant in the sun and other stars as shown by spectroscopy⁽²⁴⁾. Its abundance in the universe is estimated as 6850 atoms per million atoms Si⁽²⁵⁾. Its relatively large abundance is expected since ^{55}Mn is one of the nuclides in the iron region abundance peak⁽²⁶⁾.

Manganese does not occur as the free element in nature, but is very widespread in compounds and is an essential constituent of about 140 minerals and a minor constituent of many more⁽²⁷⁾. A few of the more important minerals are listed in Table III.1. Although manganese minerals are widespread, high grade ores are found in only a few localities, especially the U.S.S.R. (producing nearly half of the world's supply), Union of South Africa, Gabon, India, Brazil, and China⁽²⁸⁾. Low grade ores are widely distributed.

3. Industrial Chemistry of Manganese⁽²⁹⁾

Activation analysis and tracer studies are widely used in industry, so it will be useful to briefly outline the industrial uses of manganese. About 97% of the manganese consumption is for metallurgical purposes: plain carbon steel, high manganese steels, ferromanganese, manganese in pig iron, spiegeleisen,

TABLE III.1
IMPORTANT MANGANESE MINERALS (27)

Name	Chemical Composition	Color	Use
Alabandite	MnS	iron-black	
Franklinite	(Fe,Zn,Mn)Fe ₂ O ₄	iron-black	zinc ore
Manganosite	MnO	emerald-green	
Hausmannite	Mn ₃ O ₄	brown-black	manganese ore
Braunite	3Mn ₂ O ₃ ·MnSiO ₃	brown-black	manganese ore
Polianite	MnO ₂	steel-gray	manganese ore
Pyrolusite	MnO ₂ (+ trace H ₂ O)	iron-black	manganese ore
Manganite	MnOOH	iron-black	manganese ore
Pyrochroite	Mn(OH) ₂	white, darkens	
Psilomelane, Wad	impure MnO ₂ ·xH ₂ O	brown-black	manganese ore
Rhodochrosite	MnCO ₃	rose-red	manganese ore
Rhodonite	MnSiO ₃	rose	manganese ore ornamental stone
Helvite	3(Mn,Fe)BeSiO ₄ ·MnS	yellow	
Spessartite	Mn ₃ Al ₂ (SiO ₄) ₃	dark-red	semiprecious gem
Tephroite	Mn ₂ SiO ₄	flesh-red	
Piedmontite	HCa ₂ (Al,Mn) ₃ Si ₃ O ₁₃	red-brown	
Bementite	H ₁₀ Mn ₈ Si ₇ O ₂₇	gray-yellow	manganese ore
Inesite	H ₂ (Mn,Ca) ₆ Si ₆ O ₁₉ ·3H ₂ O	rose-red	
Columbite-Tantalite	(Fe,Mn)(Ta,Nb) ₂ O ₆	iron-black	Ta and Nb ore
Lithiophilite	Li(Mn,Fe)PO ₄	salmon-pink	
Triplite	(Fe,Mn)F(Fe,Mn)PO ₄	brown	
Hübnerite	MnWO ₄	brown-black	tungsten ore
Pyrophanite	MnTiO ₃	deep red	

silico-manganese, manganese in copper, aluminum, nickel, and magnesium. The remaining 3% is used in dry cells, glass making, ceramics, agriculture, and other chemical purposes⁽²⁸⁾.

The major ores of manganese are listed, along with some other manganese minerals, in Table III.1. The manganese used in iron and steel manufacture is usually in the form of a high manganese-iron alloy (ferromanganese) with up to 80% Mn, or a lower manganese-iron alloy (spiegeleisen) with 15 to 20% Mn. The alloys are produced in blast furnaces (reduction by coke). Where low carbon alloy is needed, a silicomanganese containing about 70% Mn, 20% Si, 5% Fe, and less than 1% C is produced in an electric furnace. Fairly pure manganese metal, > 97%, is produced by reduction of the oxide with silicon or aluminum, or by electrolysis of an aqueous solution of manganese salts. The electrolytic manganese is the purest commercial product with up to 99.9% Mn excluding occluded hydrogen. Electrolytic manganese is being increasingly used for the production of high grade alloys.

Manganese is an essential constituent of many copper and bronze alloys, in most commercial aluminum alloys, in certain nickel alloys, and in almost all steels. Typical low carbon steel contains about 0.2% Mn, stainless steels up to 2.5%, and some alloys up to 12%. However, for nuclear purposes steels with a minimum of manganese content are required because of the high manganese neutron capture cross section. The major functions of manganese in steel are: to combine with the sulfur to form insoluble MnS which, unlike FeS, does not cause the steel to be brittle, to deoxidize the steel, and at times to combine with carbon. Manganese, since it is much more reactive than iron, reduces the FeS, FeO, FeSiO₃, and Fe₃C in the steel and gives the corresponding manganese compounds.

Manganese compounds are important in nonmetallic products. Methyl cyclopentadienyl manganese tricarbonyl is a gasoline additive claimed to be greatly superior to tetraethyl lead⁽³⁰⁾; the substitution of nearly nontoxic manganese for lead would greatly reduce the pollution due to automobile exhaust.

Manganese at about the 0.2% level is an activator in electroluminescent phosphors; Mn and Cu in ZnS give a yellow color, Mn in zinc silicate gives a green color⁽³¹⁾. Manganese is still important in the glass industry, it is important in paints and varnishes, sometimes as a beneficial additive (drying agent), sometimes as an objectionable impurity⁽³²⁾. Manganese dioxide, which is a fairly good conductor of electricity, is an important constituent of dry cells and is also used as nonconsumable anodes for electrolysis. Manganese oxides are used as pigments. Manganese in small amounts is beneficial in fertilizers.

4. Chemical Properties of Manganese^(33,34)

Manganese is an element of the first (3d) transition series. The electronic configuration of the normal atomic state is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$, the normal state being $6S_{5/2}$. The odd number of electrons in the 3d shell results in an electronic paramagnetism, and many studies of the paramagnetic resonance of manganese have been made. The manganese resonance frequency is split into six lines, as expected, because of its $5/2$ nuclear spin, and the intensity of the lines have been used for analysis⁽³⁵⁾.

Manganese has many optical emission lines of interest in its analysis by emission spectroscopy, flame photometry, and atomic absorption. An energy level diagram of manganese has been published⁽³⁶⁾. The ionization potential of manganese is 7.41 eV for the first and 15.70 eV for the second electron.

Chemically manganese is rather similar to iron and its ions have about the same radii as the corresponding iron ions. Manganese(II) will usually isomorphously replace Fe(II) and often Mg(II). Manganese metal is considerably more reactive than iron. Trivalent manganese, although forming compounds isomorphous with those of Fe(III), is a strong oxidizing agent and is, unless complexed or insoluble, unstable disproportionating into Mn(II) and MnO_2 . In its most oxidized form, Mn(VII), manganese resembles chlorine in perchlorates, and Mn(VI), although disproportionating except in strongly alkaline solutions, resembles chromates(VI) and ferrates(VI).

Manganese exhibits all the valences from zero to seven. Under normal

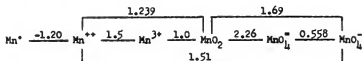
conditions only the +2, +4, and +7 are of importance. In acid solution, the Mn(II) compounds are by far the most stable, although very strong oxidizing agents such as KBrO_3 and KClO_3 will oxidize Mn^{++} to MnO_2 , and other strong oxidizing agents like KIO_4 and Ag^{++} will oxidize it to MnO_4^- . In basic solutions Mn(II) is much more easily oxidized, and even such weak oxidizing agents as $\text{Fe}(\text{CN})_6^{3-}$ and H_2O_2 will oxidize Mn(II) to MnO_2 . In basic solutions, $\text{Mn}(\text{OH})_2$ is oxidized by air first to MnOOH and ultimately to hydrated MnO_2 . The standard redox potentials for manganese, both in acid and basic solution, are given in Table III.2, and shown in Figure III.1.

TABLE III.2
STANDARD REDUCTION POTENTIALS OF MANGANESE COUPLES^(34,37)

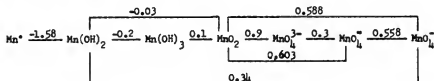
Half-cell Reaction	Oxidation States	E° volts
<u>In acid solution, H⁺ unit activity</u>		
$\text{Mn}^{++} + 2\text{e}^- \rightarrow \text{Mn}^0$	2 - 0	- 1.20
$\text{Mn}^{3+} + \text{e}^- \rightarrow \text{Mn}^{2+}$	3 - 2	- 1.5
$\text{Mn}(\text{CN})_6^{3-} + \text{e}^- \rightarrow \text{Mn}(\text{CN})_6^{4-}$	3 - 2	- 0.24
$\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Mn}^{++} + 2\text{H}_2\text{O}$	4 - 2	1.239
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{++} + 4\text{H}_2\text{O}$	7 - 2	1.51
$\text{MnO}_2 + 4\text{H}^+ + \text{e}^- \rightarrow \text{Mn}^{3+} + 2\text{H}_2\text{O}$	4 - 3	- 1.0
$\text{MnO}_4^- + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$	6 - 4	2.26
$\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$	7 - 4	1.69
$\text{MnO}_4^- + \text{e}^- \rightarrow \text{MnO}_4^{2-}$	7 - 6	0.558
<u>In basic solution, OH⁻ unit activity</u>		
$\text{Mn}(\text{OH})_2 + 2\text{e}^- \rightarrow \text{Mn}^0 + 2\text{OH}^-$	2 - 0	- 1.58
$\text{Mn}(\text{OH})_3 + \text{e}^- \rightarrow \text{Mn}(\text{OH})_2 + \text{OH}^-$	3 - 2	- 0.2
$\text{MnO}_2 + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Mn}(\text{OH})_2 + 2\text{OH}^-$	4 - 2	- 0.03
$\text{MnO}_4^- + 4\text{H}_2\text{O} + 5\text{e}^- \rightarrow \text{Mn}(\text{OH})_2 + 6\text{OH}^-$	7 - 2	0.34
$\text{MnO}_2 + 2\text{H}_2\text{O} + \text{e}^- \rightarrow \text{Mn}(\text{OH})_3 + \text{OH}^-$	4 - 3	- 0.1
$\text{MnO}_4^{3-} + 2\text{H}_2\text{O} + \text{e}^- \rightarrow \text{MnO}_2 + 4\text{OH}^-$	5 - 4	- 0.9
$\text{MnO}_4^{2-} + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{MnO}_2 + 4\text{OH}^-$	6 - 4	0.603
$\text{MnO}_4^- + 2\text{H}_2\text{O} + 3\text{e}^- \rightarrow \text{MnO}_2 + 4\text{OH}^-$	7 - 4	0.58
$\text{MnO}_4^- + \text{e}^- \rightarrow \text{MnO}_4^{2-}$	6 - 5	- 0.3
$\text{MnO}_4^{2-} + \text{e}^- \rightarrow \text{MnO}_4^{3-}$	7 - 6	0.558

FIGURE III.1
POTENTIAL DIAGRAM FOR MANGANESE⁽³⁷⁾

Acid Solution, H^+ unit activity



Basic Solution, OH^- unit activity



Manganese Metal

Manganese metal, as normally formed, is a hard brittle metal that can be powdered in a mortar. It has four allotropes, alpha and beta which are hard and brittle, gamma which is soft and ductile, and delta. The properties of manganese are summarized in Table III.3. Gamma manganese can be produced at room temperature by electrodeposition, and can be rolled into foils before it slowly converts into the stable alpha form⁽³⁸⁾. Manganese forms many alloys; alloys of Al, Mn, Sb, and Cu, Heusler alloys, are ferromagnetic. Alloys of manganese with uranium and plutonium form very low melting eutectics and have been studied for fast reactor applications^(39,40). Manganese forms many inter-metallic compounds. Chemically manganese is a highly reactive metal, reacting slowly with oxygen free cold water and more rapidly with oxygen free warm water to give $Mn(OH)_2$ and hydrogen. It is very rapidly soluble in acids, even very weak ones, giving the corresponding manganous salt. The metal burns in air and oxygen and in the halogens; above $1200^\circ C$, it burns in nitrogen forming the

TABLE III.3
PROPERTIES OF MANGANESE METAL (34)

Allotropes	Crystal Structure	Density g/cm ³	Specific Heat cal./g °C
Alpha	Body centered cubic	7.44 (20°C)	0.114
Beta	Body centered cubic	7.29 (20°C)	0.154
Gamma	Face centered tetragonal	7.18 (20°C)	0.148
Delta			0.191
Liquid		6.54	

Transition	Temperature °C	Heat of Transition cal./ g-atom
Alpha - Beta	727	535
Beta - Gamma	1100	545
Gamma - Delta	1138	530
Delta - Liquid	1245 (melting point)	3500
Liquid - Gas	2097 (760 mm boiling point)	53620
Alpha - Gas	25	67200

nitride Mn_3N_2 . Manganese forms a carbide, Mn_3C , which is isomorphous with Fe_3C and is important in steel.

Zerivalent Manganese

Manganese forms a few covalent compounds in which it is considered as exhibiting the valence of zero, the best characterized being the carbonyl, $Mn_2(CO)_{10}$, the dicyclopentadienyl manganese complex, $(C_5H_5)_2Mn$, and the cyclopentadienyl carbonyl, $C_5H_5Mn(CO)_3$. These compounds are too difficult to prepare to be of interest in radiochemical separations, but they are of interest in isotope exchange studies and in Stillard Chalmers reaction studies⁽⁴¹⁾.

Univalent Manganese

A few cyanide complexes of Mn(I) have been prepared by electrolytic reduction or the action of very strong reducing agents on manganocyanides giving $Na_5Mn(CN)_6$, $K_5Mn(CN)_6$, etc.⁽⁴²⁾. These compounds are extremely

strong reducing agents and liberate H_2 from aqueous solutions and reduce Pb^{++} and Cd^{++} to metal. A nitrosyl compound, $K_3Mn(CN)_5NO$ is also known.

Divalent Manganese

Divalent manganese has a half-filled 3d electron shell and so is particularly stable. It is both much more difficult to oxidize and reduce than Fe^{++} , although in many other ways it closely resembles Fe^{++} . The ionic radius of the Mn^{++} ion is 0.80 Å, a little larger than Fe^{++} , and as expected Mn^{++} normally forms somewhat less stable complexes than Fe^{++} . In acid solution almost any operation other than treatment with very strong oxidizing agents will yield $Mn(II)$. Manganese (II) salts are, in general, stable and usually have a pale pink color which has given the name to the minerals rhodochrosite, $MnCO_3$, and rhodonite, $MnSiO_3$. The hydroxide, $Mn(OH)_2$, is oxidized in air to the $Mn(III)$ hydroxide and ultimately to hydrated $Mn(IV)$ oxide; $Mn(OH)_2$, however, is much more stable than $Fe(OH)_2$, and is found in nature as the mineral pyrochroite. Manganous salts show a very slight tendency to hydrolyze; however in air, the hydrolysis of acid free manganous salts continues because the $Mn(OH)_2$ produced is oxidized to extremely insoluble $MnOOH$ and $MnO_2 \cdot xH_2O$. The oxide, MnO , is produced by the ignition of higher oxides in hydrogen and is stable but easily oxidized in air to Mn_3O_4 . Some $Mn(II)$ salts of interest are listed in Table III.4. Of special interest to the radiochemist are: $MnNH_4PO_4 \cdot H_2O$ which is precipitated from a NH_4OH plus NH_4Cl solution of Mn^{++} by $(NH_4)_2HPO_4$, MnS which is precipitated from an alkaline solution of Mn^{++} , even in the presence of tartrate ion, by $(NH_4)_2S$. The solubility products of a number of slightly soluble manganous compounds are given in Table III.4. The anhydrous sulfate, $MnSO_4$, is produced by igniting almost any manganese compound with H_2SO_4 ; it is a suitable weighing form for manganese. The thermodynamic properties of some manganese compounds are given in Table III.5⁽³⁷⁾.

Divalent manganese has a weak tendency to form complexes. Cyanide complexes of the type $Mn(CN)_6^{4-}$ (42) are well known but are far less stable than ferrocyanide and are very easily oxidized, even in air, to $Mn(CN)_6^{3-}$. Very weak

TABLE III.4
COMPOUNDS OF MANGANESE

SOLUBLE SALTS					
Compound	Mol. weight	How Made	Color ‡	Solubility g/100g H ₂ O	Hydrates mols H ₂ O
Manganese II Compounds					
Mn(CH ₃ COO) ₂	173.02	Mn(NO ₃) ₂ + (CH ₃ CO) ₂ O	pink(4)	40(20°C)	4
MnBr ₂	214.76	Mn oxide + HBr	rose-red(4)	144(18°C)	6,4,2
MnCl ₂	125.84	Mn oxide + HCl	rose(4)	74(20°C)	6,4,2
Mn(ClO ₄) ₂	253.84	Mn(OH) ₂ + HClO ₄		136(25°C)	6,4
MnF ₂	92.93	MnO + HF	pink(0)	1.06(25°)	4
MnI ₂	308.77	MnO + HI	rose-red(4)	sol.	9,6,4,2,1
Mn(NO ₃) ₂	178.94	Mn oxide + HNO ₃	pink(6)	134(18°C)	6,4,2,1
MnSO ₄	151.00	Mn comp. + H ₂ SO ₄	rose(5)	68(25°C)	7,5,4,2,1
K ₄ Mn(CN) ₆	367.43	MnCO ₃ + KCN	blue-violet	sol.	3
Manganese III Compounds					
Mn(CH ₃ COO) ₃	232.07	Mn(CH ₃ COO) ₂ + MnO ₄ ⁻	brown(2)	sol. acid	2
K ₂ MnCl ₅	161.30	Mn ₂ O ₃ + HCl + KCl	red-violet	sol. decomp.	
MnF ₃	111.93	MnI ₂ + F ₂	red(2)	sol. acid	2
K ₃ Mn(CN) ₆	328.33	K ₄ Mn(CN) ₆ + air	dark red	sol. acid	
K ₃ Mn(C ₂ O ₄) ₃	436.30	H ₂ C ₂ O ₄ + MnO ₄ ⁻ + CO ₃ ²⁻	red(3)	v. sol.	3
CaMn(SO ₄) ₂	379.98	Ca ₂ SO ₄ + Mn(CH ₃ COO) ₃ + H ₂ SO ₄	cerise red(12)	sol. acid	12
Manganese IV Compounds					
K ₂ MnCl ₆	345.86	KMnO ₄ + con. HCl	dark red	sol. decomp.	
K ₂ MnF ₆	247.12	MnO ₂ + HF	gold-yellow	sol. acid	
Manganese VI Compound					
K ₂ MnO ₄	197.12	MnO ₂ + KOH + KNO ₃	dark green	sol. KOH	
Manganese VII Compounds					
NH ₄ MnO ₄	136.97		purple	7.9(15°C)	
Ca(MnO ₄) ₂	277.94		purple(9)	250(25°C)	9
HMnO ₄	119.94	evap. frozen sol'n.	dark purple	sol.	2
KMnO ₄	158.03	K ₂ MnO ₄ + Cl ₂ + H ⁺	dark purple	6.34(20°C)	
AgHMnO ₄	226.81		dark violet	0.92(20°C)	
NaMnO ₄	141.93		purple(3)	v. sol.	3

‡ Color of hydrate with () moles of H₂O

INSOLUBLE SALTS

Compound	Mol. weight	How Made	Color	Solubility product
Manganese II Compounds				
$MnCO_3$	114.94	neutral $Mn^{++} + CO_3^{--}$	pink	$8.8 \times 10^{-11} (25^\circ C)$
$Mn_2Fe(CN)_6 \cdot 7H_2O$	447.93	$Mn^{++} + Fe(CN)_6^{4-}$	green-white	$7.9 \times 10^{-13} (25^\circ C)$
$Mn(OH)_2$	88.95	$Mn^{++} + OH^-$	white, turns brown	$1.6 \times 10^{-13} (22^\circ C)$
$Mn(IO_3)_2$	404.77	$Mn^{++} + IO_3^-$		$4.8 \times 10^{-7} (25^\circ C)$
$MnC_2O_4 \cdot 2H_2O$	178.98	$Mn^{++} + C_2O_4^{--}$	pink	$\sim 10^{-13}$
MnO	70.93	$Mn_3O_4 + H_2$ heated	green	
$Mn_3(PO_4)_2 \cdot 7H_2O$	480.86	neutral $Mn^{++} + HPO_4^{--}$	pink	$\sim 10^{-22}$
$MnNH_4PO_4 \cdot H_2O$	185.97	$Mn^{++} + NH_4OH + HPO_4^{--}$	pink	
$Mn_2P_2O_7$	283.82	ignite $MnNH_4PO_4 \cdot H_2O$	pink	
$MnSiO_3$	130.99	$MnO + SiO_2$ fused	red	
Mn_2SiO_4	201.92	$2MnO + SiO_2$ fused	pink	
MnS	87.00	$Mn^{++} + (NH_4)_2S$	flesh	$2 \times 10^{-13} (25^\circ C)$
Manganese III Compounds				
$MnOOH$	87.94	$Mn(OH)_2 + O_2$	brown	$\sim 10^{-42}$
Mn_3O_4	228.79	ignite oxides at $1000^\circ C$	red	
Mn_2O_3	157.86	ignite oxides at $700^\circ C$	black	
$MnPO_4 \cdot H_2O$	167.93	$Mn(CH_3COO)_3 + H_3PO_4$	gray-green	
Manganese IV Compounds				
$MnO_2 \cdot xH_2O$		$Mn^{++} + BrO_3^-$ or ClO_3^-	brown-black	very insoluble
MnO_2	86.93	decomp. $Mn(NO_3)_2$ $250^\circ C$	black	
Manganese VI Compound				
$BaMnO_4$	256.29	basic $Ba^{++} + MnO_4^{--}$	gray-green	1.5×10^{-10}
Manganese VII Compound				
$CsMnO_4$	251.84	$Cs^+ + MnO_4^{--}$	purple	1.5×10^{-5}

VOLATILE COMPOUNDS					
Compound	Mol. weight	How made	Color	Melting point °C	Boiling point °C
Mn_2O_7	221.86	$KMnO_4$ + con. H_2SO_4	red	-33°	70° explodes
$Mn(C_5H_7O_2)_3$	352.25	acetylacetone + $Mn(CH_3COO)_3$	green-black	172°	volatile
$Mn_2(CO)_{10}$	389.96		gold	154°	
$C_5H_5Mn(CO)_3$	204.05		yellow	77°	volatile
$(C_5H_5)_2Mn$	185.11		amber	172°	245°

TABLE III.5
THERMODYNAMIC DATA FOR MANGANESE COMPOUNDS (37)
298°K

Compound	ΔH kcal/mol.	ΔG kcal/mol.	ΔS cal/mol., °C
$Mn(s, \alpha)$	0	0	7.64
$Mn(g)$	67.2	57.1	41.49
$Mn^{2+}(H_2O)$	-53.2	-55.1	-17
$MnO(s)$	-92.0	-86.7	14.3
$Mn_3O_4(s)$	-331.3	-306.2	36.8
$Mn_2O_3(s)$	-228.7	-210.1	26.4
$MnO_2(s)$	-124.4	-111.3	12.68
$Mn(OH)_2(s)$	-167	-148	23
$MnF_2(s)$	-190	-179	22.25
$MnCl_2(s)$	-115.6	-105.9	28.26
$MnBr_2(s)$	-92.6	-89	33
$MnI_2(s)$	-64.2	-65	37
$MnS(s)$	-49.5	-50.5	18.7
$MnSO_4(s)$	-254.9	-229.1	26.8
$MnCO_3(s)$	-214	-196	20.5
$KMnO_4(s)$	-200.6	-176.8	41.0
$Mn_2(CO)_{10}(s)$	-400.9		

chloride complexes are known, MnCl_3^- , MnCl_4^{2-} , and MnCl_6^{4-} , the latter being stable enough to be weakly absorbed on anion resins from very strong HCl. Mn(II) forms a number of chelate complexes, see Table III.6, for example, the Mn(II) chelate with ethylenediaminetetraacetic acid which is of importance in analytical chemistry. Divalent manganese forms complexes with acetylacetone and oxalic acid. Manganese (II) forms double sulfates, nitrates, and halides with a number of metals; these compounds are very weak complexes if they are true complexes at all. Mn(II) can form amine complexes, e.g. $\text{Mn}(\text{NH}_3)_6^{2+}$, but the complexes are not stable in aqueous solution.

TABLE III.6
STABILITY CONSTANTS OF MANGANESE COMPLEXES^(34,37)

Reaction	$\log_{10}$ Equilibrium constant
$\text{Mn}^{2+} + \text{H}_2\text{O}(l) \rightarrow \text{MnOH}^+ + \text{H}^+$	-10.59
$\text{Mn}^{2+} + \text{F}^- \rightarrow \text{MnF}^+$	0.79
$\text{Mn}^{2+} + \text{Cl}^- \rightarrow \text{MnCl}^+$	0.59
$\text{Mn}^{2+} + \text{SO}_4^{2-} \rightarrow \text{MnSO}_4$	2.26
$\text{Mn}^{2+} + \text{C}_2\text{O}_4^{2-} \rightarrow \text{MnC}_2\text{O}_4$	3.89
$\text{Mn}^{2+} + \text{malonate} \rightarrow \text{Mn}(\text{OOCCH}_2\text{COO})$	3.29
$\text{Mn}^{2+} + 2 \text{ acetylacetone} \rightarrow \text{Mn}(\text{CH}_3\text{COCHCOCH}_3)_2$	9.96
$\text{Mn}^{2+} + \text{EDTA}^{4-} \rightarrow \text{MnEDTA}^{2-}$	13.4
$\text{Mn}^{3+} + \text{H}_2\text{O}(l) \rightarrow \text{MnOH}^{2+} + \text{H}^+$	-0.056
$\text{Mn}^{3+} + \text{F}^- \rightarrow \text{MnF}^{2+}$	2.48
$\text{Mn}^{3+} + \text{Cl}^- \rightarrow \text{MnCl}^{2+}$	0.96
$\text{Mn}^{3+} + \text{C}_2\text{O}_4^{2-} \rightarrow \text{MnC}_2\text{O}_4^+$	9.98
$\text{Mn}^{3+} + 2\text{C}_2\text{O}_4^{2-} \rightarrow \text{Mn}(\text{C}_2\text{O}_4)_2^-$	16.6
$\text{Mn}^{3+} + 3\text{C}_2\text{O}_4^{2-} \rightarrow \text{Mn}(\text{C}_2\text{O}_4)_3^{3-}$	19.42

Trivalent Manganese

Simple, uncomplexed Mn^{3+} in solution disproportionates into Mn^{++} and MnO_2 ; however, $Mn(III)$ forms a number of complexes and insoluble compounds that are stable. Some compounds of $Mn(III)$ are listed in Table III.4. The oxide, Mn_2O_3 , and the "ous-ic" oxide, Mn_3O_4 , are stable, the latter compound being the usual, but somewhat uncertain, weighing form for manganese. $Mn(III)$ forms a moderately stable manganicyanide, $Mn(CN)_6^{3-}$ (42), which is much more difficult to reduce than $Fe(CN)_6^{3-}$ and also shows a tendency to hydrolyze in water. A phosphate complex, $Mn(H_2P_2O_7)_3^{3-}$, is important in analytical chemistry. $Mn(III)$ forms fluoro, chloro, and sulfato (alum) complexes. It forms a number of organic complexes, see Table III.6. $Mn(III)$ complexes are normally red to violet, and even the complexes tend to hydrolyze and disproportionate and are usually strong oxidizing agents. The ion, Mn^{3+} , is considered to have the greatest tendency to hydrolyze of any trivalent cation⁽³⁷⁾.

Tetavalent Manganese

The only readily obtainable compound of $Mn(IV)$ is the extremely insoluble dioxide which is insoluble in almost any aqueous medium which does not reduce it. The hydrated dioxide is the form in which manganese is precipitated in many radiochemical separations by the addition of a strong oxidizing agent such as $KBrO_3$ or $KClO_3$ to a nitric acid solution of Mn^{++} . The dioxide is also precipitated as a scavenger during the processing of irradiated uranium fuel by the addition of first Mn^{++} , then MnO_4^- . Anhydrous MnO_2 , formed by the thermal decomposition of $Mn(NO_3)_2$ is stable to above $500^\circ C$; hydrated MnO_2 , however, may start to decompose at a temperature as low as $200 - 300^\circ C$. MnO_2 dissolves in strong HCl to give a dark colored $Mn(IV)$ chloro complex which gradually decomposes to Mn^{++} and Cl_2 . $Mn(IV)$ forms some fluoro and chloro complexes such as K_2MnF_6 and K_2MnCl_6 , and also some iodate complexes of the anion $Mn(IO_3)_6^{4-}$. Hydrated MnO_2 reacts with strong alkalis to form insoluble manganites such as $K_2Mn_2O_5$.

Pentavalent Manganese

Manganese forms a few compounds in which it exhibits a valence of five. The recently synthesized MnOCl_3 ⁽⁴³⁾ and KMnO_3 are examples.

Hexavalent Manganese

Manganates, e.g. K_2MnO_4 , can be prepared by fusing MnO_2 with KOH and KNO_3 . They are stable in strongly alkaline solutions, but disproportionate to MnO_2 and MnO_4^- in weakly alkaline, neutral, or acidic solutions. The MnO_4^- ion is green. A manganyl chloride, MnO_2Cl_2 , has been recently prepared⁽⁴³⁾.

Heptavalent Manganese

Seven is the group valence of manganese. Mn(VII) forms the strongly oxidizing but stable MnO_4^- ion which is of great importance in radiochemistry and analytical chemistry. KMnO_4 is usually prepared by fusing MnO_2 with KOH in air or with KOH and KNO_3 , then treating the resulting manganate with H_2SO_4 plus at times oxidation with Cl_2 . Permanganates are deep purple and strong oxidizing agents. The acid, HMnO_4 , is a strong acid like HClO_4 and has recently been prepared as a solid crystalline compound by the vacuum evaporation of a frozen solution⁽⁴⁴⁾. The oxide, Mn_2O_7 , has been isolated and can be distilled, usually with considerable decomposition. The distillation of Mn_2O_7 is the basis of a radiochemical separation for manganese.

Pernganyl chloride, MnO_3Cl , has been synthesized⁽⁴³⁾. Permanganates can be produced from Mn^{++} in acid solution by oxidation with periodate, persulfate plus Ag^+ catalyst, Ag^{++} , PbO_2 , and sodium bismuthate. Permanganate can be extracted with alkaline pyridine and alkaline $(\text{C}_6\text{H}_5)_4\text{AsCl}$ in CHCl_3 . Data on some common permanganates are included in Table III.4. Permanganates are isomorphous with perchlorates, persulfates, and pertechnetates. Permanganate solutions are relatively stable, especially if free of MnO_2 , and are used extensively as standard oxidizing solutions in analytical chemistry.

When heated, KMnO_4 is first decomposed at about 200°C to K_2MnO_4 and MnO_2 , then at higher temperatures to Mn_2O_3 and Mn_3O_4 .

5. Analytical Chemistry of Manganese ⁽³⁴⁾

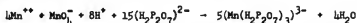
Manganese is a member of the third group in the standard qualitative analysis scheme and is characterized by a sulfide, MnS , insoluble in basic solutions, and a hydroxide, $Mn(OH)_2$, which, while insoluble in NH_4OH alone, is soluble in NH_4OH plus excess NH_4^+ salts and which is slowly oxidized in air to an insoluble hydrated oxide of $Mn(III)$ or $Mn(IV)$. The final test for manganese is usually its oxidation to purple permanganate.

Emission spectroscopy is an excellent method for detecting and making semiquantitative determinations of manganese ⁽⁴⁵⁾; X-ray fluorescence can also be used. Permanganate ion has a strong infrared absorption band in the eleven micron region and infrared has been used for the identification of the ion. Many extremely sensitive spot tests are known for detecting microgram or smaller quantities of manganese ⁽⁴⁶⁾. The most common test is based upon the oxidation to MnO_4^- by various oxidizing agents. An extremely sensitive, although not very specific test, is based upon the oxidation of benzidine to a blue color by the MnO_2 produced by air oxidation of alkaline $Mn(OH)_2$. Another sensitive test (0.001 μg Mn in one drop) is based upon the oxidation of "tetrabase" (tetramethyl p-diaminodiphenylmethane) to a blue oxidation product by periodate with manganese serving as a catalyst. A third sensitive (0.05 mg/liter) and fairly specific test has been developed in which manganese produces an intense red-violet color with an alkaline solution of formaldoxime.

Manganese can be determined quantitatively by a number of methods. The most convenient method is a photometric method based upon the oxidation of manganese to MnO_4^- with KIO_4 or some other oxidizing agent. If a narrow band spectrophotometer is used to measure the absorbance, a precision of 0.5% standard deviation over a wide range of manganese concentration can be obtained and as little as 2 μg Mn in 50 ml. can be detected ⁽⁴⁷⁾. The method is virtually free of interferences. Because the method is commonly used to determine manganese yields in radiochemical separations, it is included with the radiochemical separation procedures in section VI. A number of other photometric

methods have been developed based upon either the color of Mn(III) complexes or on the colors produced in organic reagents due to oxidation by manganese compounds. Activation analysis is also widely used to determine manganese, and several separation schemes are included in section VI.

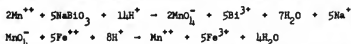
Several titrimetric methods, based upon oxidation-reduction, are widely used for manganese. A widely used method is based upon the titration of Mn(II) with standard permanganate in a neutral pyrophosphate solution⁽⁴⁸⁾. The reaction is:



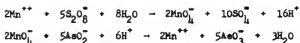
Since the Mn(III) complex is intensely colored, the endpoint is determined potentiometrically. The method is virtually free of interference. Manganese (II) can also be titrated with MnO_4^- in a nearly neutral solution (Volhard method) according to the reaction:



The endpoint is determined by observing the appearance of purple MnO_4^- . The reaction is not quite stoichiometric and the end point is difficult to observe visually because of the precipitate of MnO_2 . The classical titrimetric method is based upon the oxidation of Mn^{++} to MnO_4^- with sodium bismuthate, then removal of the excess bismuthate by filtration and reduction of the permanganate with standard ferrous ammonium sulfate⁽⁴⁹⁾. The reactions are:



Most commonly an excess of standard Fe^{++} is added and the excess titrated with standard permanganate, ferrous o-phenanthroline or the appearance of the purple of MnO_4^- being the indicator. A large number of materials including cerium, cobalt, chromium, nitrous acid, fluoride, and chloride interferes. As an alternate procedure, the permanganate can be treated with standard arsenite. Another titrimetric method is based upon the oxidation of the Mn^{++} in boiling $\text{H}_2\text{SO}_4 - \text{H}_3\text{PO}_4$ solution with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and Ag^+ catalyst, then titration of the MnO_4^- with standard arsenite. The reactions are:



The end point can be determined by the disappearance of the purple MnO_4^- color or potentiometrically. Fewer elements interfere than with the Fe^{++} titration. Manganese can be determined by titration with ethylenediaminetetraacetic acid using Eriochrome Black T as the indicator. Complexing with cyanide will prevent interferences by Hg, Cd, Co, Zn, Cu, Ni, and Fe.

Manganese is determined quantitatively by emission spectroscopy, flame photometry, atomic absorption, and X-ray fluorescence⁽⁵¹⁾. It can be determined polarographically. A number of gravimetric methods have been developed but are seldom used because other methods are much faster and less subject to interference. The gravimetric methods make use of the precipitation of manganese as $\text{MnNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$, MnS , and MnO_2 and ignition to $\text{Mn}_2\text{P}_2\text{O}_7$, MnSO_4 , or Mn_3O_4 ; all of these precipitation methods have been used in radiochemical separations.

6. Dissolution of Manganese Sample⁽³⁴⁾

Inorganic Materials

The dissolution of manganese minerals and ores can often be accomplished by acid attack followed by KHSO_4 or Na_2CO_3 fusion of the insoluble residue. The dissolution of MnO_2 is greatly facilitated by the addition of a reducing agent such as H_2O_2 or SO_2 . The dissolution method is often dictated by what other elements are present in the sample and what elements in addition to manganese are being determined.

Manganese metal is very readily soluble in dilute acids. Most steels and cast irons can be dissolved in HNO_3 , HCl , H_2SO_4 , or aqua regia. Tungsten steels may require H_3PO_4 . Some high temperature alloys containing major amounts of Ni, Co, Cr, W, and Nb are very difficult to dissolve and may require fusion with Na_2O_2 or anodic electrolytic attack. An interesting dissolution technique for analyzing inclusions in steel is the solution of the metal in cold FeI_2 solution which leaves the oxide inclusions, FeO , MnO , SiO_2 , Al_2O_3 , etc. unattacked⁽⁵⁰⁾.

Organic Materials

Biological samples are usually either wet or dry ashed before analyzing for manganese. Ignition of dried plant material, grain, feeds, fruit, etc., at about 525°C in a porcelain or platinum crucible and digestion of fertilizers with H_2SO_4 and HNO_3 is recommended by the Association of Official Agricultural Chemists⁽⁵²⁾. Wet oxidation is becoming more popular for destroying organic matter. Biological materials, grasses, feces, body tissues, etc., are boiled with HNO_3 in a Kjeldahl flask then finally fumed with HNO_3 plus HClO_4 ; dye intermediates and rubber chemicals are treated with H_2SO_4 , HNO_3 , and H_2O_2 . Petroleum and petroleum distillates are wet ashed preparatory to analysis for manganese and other trace metals; $\text{HNO}_3 + \text{H}_2\text{SO}_4$ digestion is used for analyzing paint driers for manganese. Manganese organometallic compounds, e.g. gasoline additives, are decomposed by ultraviolet radiation, bromine oxidation, and sometimes by water alone.

7. Separation of Manganese⁽³⁴⁾

Precipitation Methods

The most generally used and quite specific method for separating manganese is its precipitation as hydrated MnO_2 from a boiling HNO_3 solution of Mn^{++} by adding bromate, chlorate, or persulfate oxidizing agent. The MnO_2 so formed carries Si, W, Ta, Nb, and Pa nearly quantitatively and often is also contaminated with Zr, Fe, Sb, and other elements which hydrolyze easily. The MnO_2 precipitation is usually not quite quantitative. Precipitation of MnO_2 may be made from nearly neutral solutions by oxidation with Br_2 . Manganese, even at trace level, can be electrodeposited on the anode as MnO_2 ⁽⁵³⁾.

Iron (III), aluminum, zirconium, and other elements with very insoluble hydroxides can be precipitated with NH_4OH in the presence of excess ammonium salts, leaving Mn(II) in solution. Some manganese is usually precipitated since the Mn(II) is air oxidized to very insoluble $\text{Mn}(\text{OH})_3$; however, the air oxidation can be prevented by the addition of hydroxylamine hydrochloride to the solution. After filtering or centrifuging out the insoluble hydroxides,

manganese can be precipitated from the same solution by the addition of an oxidizing agent, e.g. H_2O_2 .

The precipitation of manganese as MnS from a slightly basic solution of $\text{Mn}^{++} + \text{NH}_4^+$ with H_2S or $(\text{NH}_4)_2\text{S}$ will separate manganese from alkaline earths. The acid insoluble sulfides, including ZnS , can be first precipitated from a weak acetic acid solution. The precipitation of MnO_2 with NaOH plus H_2O_2 will separate manganese from Al , Cr , Mo , V , and other amphoteric elements which form alkali soluble salts. Many elements, Fe , Ni , Cu , Zn , Cr , etc., can be separated from Mn by quantitative deposition in a mercury cathode; under properly controlled conditions, Mn can also be quantitatively deposited.

Other precipitation separations are sometimes used: Fe(III) , Ti , Zr , and V can be precipitated with cupferron leaving Mn in solution, $\text{MnNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ can be precipitated from citrate solutions leaving Co in solution, CoS and NiS can be precipitated in the presence of pyridine leaving Mn in solution, Fe(III) can be precipitated as a basic formate using urea with Mn remaining in solution. Complexing with EDTA and other chelates prevents the precipitation of Mn during the hydrolytic precipitation of Nb and Ta . Fe(III) can be precipitated with pyridine leaving Mn in solution.

Manganese(VII) can be separated by precipitation as tetraphenylarsonium permanganate. Perchlorate, perrhenate, etc., can be precipitated before the manganese is oxidized to MnO_4^- .

Volatilization Methods

Manganese, as Mn_2O_7 , can be slowly distilled from 10 M H_2SO_4 containing HIO_4 (55).

Solvent Extraction

Solvent extraction has been extensively studied as a method for separating manganese. Manganese does not form very many extractable complexes, and often other elements are extracted away from the manganese, e.g. Fe(III) from HCl with ether. Since manganese exists in several valences, it is often possible to adjust the valence so manganese will or will not extract. Several solvent

extraction separations for manganese are given below:

a. Pyridine⁽⁵⁶⁾

Add pyridine to a solution containing MnO_4^- , shake, add 4 N NaOH, shake a few seconds and centrifuge. MnO_4^- extracts. Speed is essential since pyridine slowly reduces MnO_4^- to nonextractable MnO_2 . ReO_4^- and TeO_4^- also extract.

b. 8-Quinolinol (8-hydroxyquinoline)⁽⁵⁶⁾

Take 50 ml of solution with up to 0.2 mg Mn and 10 ml 10% NaK tartrate, adjust to pH 7.5 - 12.5. Shake 1 min with 10 ml 1% 8-quinolinol in CHCl_3 . Mn(II) complex extracts; Fe and Cu interfere.

c. Tetraphenylarsonium Chloride^(56,57)

Make the solution alkaline with NaOH. Oxidize Mn to MnO_4^- with $\text{K}_2\text{S}_2\text{O}_8$. Add 1% $(\text{C}_6\text{H}_5)_4\text{AsCl}$ solution to make solution about $5 \times 10^{-5}\text{M}$. Extract 5 min. with an equal volume of CHCl_3 ; Mn extracts quantitatively as $(\text{C}_6\text{H}_5)_4\text{AsMnO}_4^-$. ReO_4^- , TeO_4^- , ClO_4^- also extract, but can be removed by extraction before the manganese is oxidized.

d. Diethyldithiocarbamate⁽⁵⁸⁾

Use 175 ml of solution with some citric acid, adjust the pH to about 5.3, add 0.4 g Na diethyldithiocarbamate (DIECA), adjust pH again to 5.4, and extract with 25 ml CHCl_3 , readjusting the pH by adding HCl.

e. Thenoyltrifluoroacetone⁽⁵⁹⁾

Manganese(II) TTA complex can be extracted from fairly high pH solutions. Buffer the solution with $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ plus NaOH to give a pH of 8.0 - 8.5. Add a little hydroxylamine hydrochloride to prevent air oxidation of Mn(II). Add a little TTA (0.1 M in alcohol) and extract with ethyl acetate for 2 to 3 minutes.

Many other solvent extraction systems have been used for extracting manganese and separating unwanted elements from manganese. The separation of Fe and Mn by thiocyanate extraction with tributylphosphate has been studied⁽⁶⁰⁾; 1-phenyl-3-methyl-4-hexyl-pyrazolone-5 has been used to complex Mn (depending upon pH) so that it will extract into methylisobutyl ketone⁽⁶¹⁾. Octyl- α -anilinobenzylphosphonate in ligroin has been used to extract Mn from H_2SO_4

solution⁽⁶²⁾. The long chain amine, alamine 336, has been used to extract manganese from solutions highly salted with LiCl, etc.⁽⁶³⁾. Cupferron has been used to extract manganese⁽⁶⁴⁾. Dithizone has been used to quantitatively extract trace Mn from seawater⁽⁶⁵⁾. Manganese has been extracted from a pH 2.7 solution by di-(2-ethylhexyl) phosphoric acid in hexane⁽⁶⁶⁾.

Ion Exchange

Divalent manganese in strong HCl is weakly absorbed on strong base anion exchange resin, and manganese can thus be separated from those ions that are not absorbed at all (Cr^{3+} , Al^{3+} , Tl^+ , Ni^{++} , and trivalent rare earths) and those ions that are strongly absorbed (Fe^{3+} , UO_2^{++} , WO_4^{--} , Co^{++} , Ti^{3+} , and noble metals)⁽⁶⁷⁾. Anion exchange separations have been worked out in other media, oxalic acid⁽⁶⁸⁾, acetone plus HCl in water⁽⁶⁹⁾, ethanol plus HCl in water⁽⁷⁰⁾. Because Mn^{++} is normally so weakly absorbed, the separations are not very useful for concentrating manganese. A weakly basic anion resin has been used to concentrate Mn^{++} in natural waters prior to analysis⁽⁷¹⁾.

Divalent manganese is quite strongly adsorbed on cation exchange resins. Cation resins (sulfonic acid type) have been used to concentrate manganese from dilute NH_4Cl plus $(\text{NH}_4)_2\text{HPO}_4$ solutions⁽⁷²⁾. In general, cation resins have not been widely used to separate and concentrate manganese.

A chelating resin, Chelex 100, has been used to concentrate manganese and many other trace elements from seawater⁽⁷³⁾.

Other Chromatographic Separations

A number of other chromatographic separation methods have been used for manganese. Paper chromatography⁽⁷⁴⁾ has been used to separate manganese and other elements for both radiochemical and analytical purposes. The manganese is detected by the formation of insoluble $\text{Mn}_3(\text{PO}_4)_2$ (containing ^{32}P) in the paper⁽⁷⁵⁾. Metal TTA complexes have been used with solvents containing CH_3OH , C_6H_6 , and glacial CH_3COOH ⁽⁷⁶⁾ to separate Mn from Fe, Co, Ni, and Cu; 80% methyl-n-propyl ketones, 10% acetone, and 10% HCl, also, acetone plus 5% H_2O and 8% HCl have been used as solvents⁽⁷⁴⁾.

Partition chromatography has been rather more extensively studied. A column made up of CCl_4 -dithizone solution supported on cellulose acetate has been used to separate manganese from natural waters⁽⁷⁷⁾. The manganese is eluted with 1 M HCl. Ksf F supported tri-n-octylphosphine oxides⁽⁷⁸⁾ and teflon supported tri-n-octylamine⁽⁷⁹⁾ have also been used.

8. Szilard Chalmers Reactions with Manganese

Because of the use of permanganate solutions and the Szilard Chalmers concentration of the ^{56}Mn on MnO_2 for the standardization of weak neutron sources, many studies have been made of the partition of manganese activity between the MnO_2 decomposition product and the unaltered MnO_4^- ⁽⁸⁰⁾. The activity is almost all collected on the MnO_2 if the pH of the solution is less than about 11. Even when solid KMnO_4 is irradiated, only about 35% of the activity is retained with the MnO_4^- if the salt is dissolved in a solution with a pH of less than 11. Szilard Chalmers reactions have been recently studied in dilute solutions of $\text{Mn}_2(\text{CO})_{10}$ and $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3$ ⁽⁸¹⁾, and on crystalline $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3$ ⁽⁸²⁾.

Radioisotope exchange has been used to study the structure of $\text{Mn}(\text{CN})_5\text{NO}^{3-}$ ⁽⁸³⁾.

IV HAZARDS AND PRECAUTIONS

Manganese is relatively nontoxic in most of its compounds, and very few cases of manganese poisoning are known⁽⁸⁴⁾. However, workers exposed to large concentrations of manganese containing dust have been known to be poisoned. Manganism in its earliest stages results in muscular incoordination, general lassitude and sleepiness, and certain emotional disturbances such as uncontrollable laughter or crying. If the exposure to the manganese dust is continued, the poisoning will cause permanent crippling but apparently does not shorten the life span. An average concentration of 6 mg. of manganese per cubic meter of air is considered safe for an eight hour work day. Relatively large doses of manganese compounds taken orally are required to cause poisoning.

Manganese is an important trace constituent of food and the normal daily intake is about 10 mg. Activation analysis has been used to compare the manganese contents of different body fluids in normal people and people suffering from manganese poisoning⁽⁸⁵⁾. Since manganism results from exposures to large quantities of dust, the handling of normal laboratory amounts of manganese is essentially without chemical hazard. Certain manganese compounds, e.g. Mn_2O_7 and NH_4MnO_4 , are explosive.

A major hazard in the radiochemical studies of manganese is the radiation due to ^{56}Mn . Since manganese has a relatively high cross section and ^{56}Mn has a fairly short half life and many abundant gamma rays, quite large activities which give off large gamma doses are easily produced. Any sample containing manganese and irradiated in a moderate neutron flux should be very carefully surveyed before any work is started. The gamma rays from ^{56}Mn are difficult to shield. A sample of about 50 mg. Mn irradiated for 2 1/2 hours in a flux of 10^{13} n/cm²sec. will give a gamma dose, unshielded, of about 1 R/hr. at one foot (30 cm.).

As ingestion hazards, ^{52}Mn , ^{54}Mn , and ^{56}Mn are roughly equal. The recommended maximum permissible concentration of both soluble and insoluble forms in air and water are given in Table IV.1⁽⁸⁶⁾. Some recent studies of the biological half life of radiomanganese in man show two half lives, one of about four days (30% of the Mn) and one of about 39 days (70% of the Mn)⁽⁸⁷⁾.

Any work with radioactive substances should be carefully planned and proper safety precautions taken. Samples should be adequately monitored and care taken to prevent the spread of contamination. A good reference on safety procedures is included in the Oak Ridge Master Analytical Manual⁽⁸⁸⁾.

TABLE IV.1

MAXIMUM PERMISSIBLE CONCENTRATIONS OF MANGANESE ISOTOPES⁽⁸⁶⁾

Isotope		Body Burden μCi	40hr. week		168hr. week	
			in H ₂ O μCi/cm ³	in air μCi/cm ³	in H ₂ O μCi/cm ³	in air μCi/cm ³
⁵² Mn	sol.	5	10 ⁻³	2x10 ⁻⁷	3x10 ⁻⁴	7x10 ⁻⁸
5.6 d.	insol.		9x10 ⁻⁴	10 ⁻⁷	3x10 ⁻⁴	5x10 ⁻⁸
⁵⁴ Mn	sol.	20	4x10 ⁻³	4x10 ⁻⁷	10 ⁻³	10 ⁻⁷
303 d.	insol.		3x10 ⁻³	4x10 ⁻⁸	10 ⁻³	10 ⁻⁸
⁵⁶ Mn	sol.	2	4x10 ⁻³	8x10 ⁻⁷	10 ⁻³	3x10 ⁻⁷
2.6hr.	insol.		3x10 ⁻³	5x10 ⁻⁷	10 ⁻³	2x10 ⁻⁷

V COUNTING TECHNIQUES

All of the radioactive isotopes of manganese except 1.9×10^6 year ^{53}Mn decay by the emission of gamma rays of high abundance, so gamma counting, either with NaI(Tl) crystals or Ge(Li) detectors is the most commonly used method of determination. The isotopes can also be counted using Geiger Muller or flow proportional counters. An excellent discussion of counting techniques is given in the monograph by O'Kelley⁽⁸⁹⁾ and the book by Johnson, Eichler, and O'Kelley⁽⁹⁰⁾.

R. L. Heath⁽⁹¹⁾ gives scintillation gamma ray spectra of most of the radioactive nuclides including 5.6 day ^{52}Mn , 303 day ^{54}Mn , and 2.576 hour ^{56}Mn . His scintillation spectra of ^{52}Mn and ^{54}Mn are included in this monograph as Figures V.1 and V.2. A scintillation spectrum of ^{56}Mn , taken at a somewhat greater source to detector distance in order to minimize sum peaks, is given as Figure V.3. Heath also describes methods of absolute counting using scintillation counters and gives counting efficiencies, peak to total ratios, and absorption corrections for gamma rays of different energies and for different counter geometries. The total gamma emission rate (photons per unit time) is determined by dividing the integrated area of the photopeak (counts) by the

counting time, the counting efficiency at the known geometry, and the peak to total ratio. Corrections also need to be made for the fraction of the gamma ray transmitted through all absorbing material such as added beta absorber, crystal housing, and if the sample is thick, the sample itself. By using Heath's efficiency curves, absolute gamma emission rates can be determined to better than 5% standard deviation. Since 7.6 cm x 7.6 cm (3" x 3") cylindrical crystals and 10 cm source to detector distances are rather standard, Heath's values of the overall counting efficiency and the peak to total ratios for some of the manganese gamma rays are given in Table V.1. Heath gives the values for other size crystals and source to detector distances⁽⁹¹⁾.

TABLE V.1
COUNTING EFFICIENCIES FOR MANGANESE GAMMA RAYS USING A
7.6 cm x 7.6 cm CYLINDRICAL NaI(Tl) CRYSTAL
AND A 10 cm SOURCE TO CRYSTAL DISTANCE⁽⁹¹⁾

Isotope	Gamma Ray Energy MeV	Peak to Total Ratio	Gamma Counting Efficiency
Positron Emitters	0.511	0.641	0.3217
2 min. ⁵⁰ Mn	0.783(100%)	0.492	0.0192
	1.11 (100%)	0.395	0.0174
5.60 day ⁵² Mn	0.744(82%)	0.506	0.0195
	0.935(84%)	0.440	0.0183
	1.434(100%)	0.335	0.0161
303 day ⁵⁴ Mn	0.835(100%)	0.474	0.0189
2.576 hour ⁵⁶ Mn	0.848(99%)	0.470	0.0188
	1.811(29%)	0.290	0.0152
	2.110(15%)	0.262	0.0146

FIGURE V.2
GAMMA SPECTRUM OF ^{54}Mn (91)

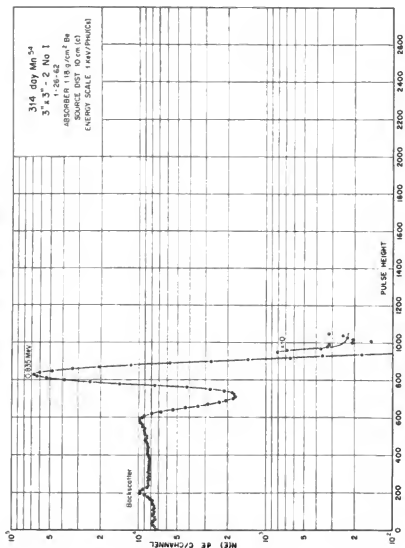
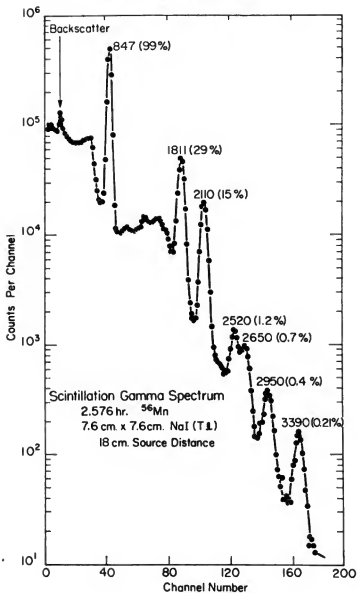


FIGURE V.3
GAMMA SPECTRUM OF ^{56}Mn



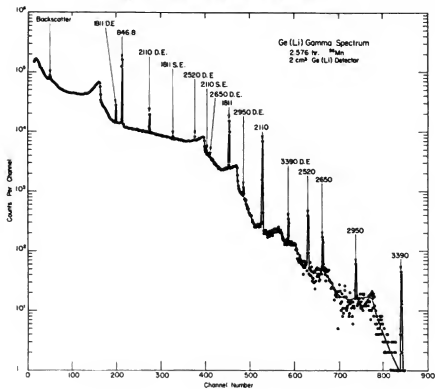
The most accurate method of determining the amount of an isotope by gamma counting is by comparison with a standard; relative gamma activities can be determined to better than 1%. The most accurate determinations also require radiochemically pure samples. However, by using scintillation counting it is often possible to resolve the composite spectrum of several nuclides into those of the individual components; thus, it is often possible to determine ^{56}Mn accurately in impure samples. Computer resolution of composite scintillation spectra is commonly done especially for routine analysis⁽⁹²⁾.

The use of high resolution lithium drifted germanium detectors has made the accurate determination of gamma emitters in impure samples much easier and more accurate⁽⁹³⁾. Typical Ge(Li) detectors are much smaller than NaI(Tl) crystals and thus have much smaller counting efficiencies. Also, germanium has a lower atomic number than iodine so that the ratio of the photoelectric process to the Compton process is smaller. However, the much higher resolution of the Ge(Li) counters makes the gamma ray photo peaks stand up much more clearly above the general background due to the Compton effect. Thus gamma rays with relatively minor abundances can be easily detected and often have their absolute counting rates determined with fair precision. The peak counting efficiency (integrated counting rate in the photo peak divided by the gamma emission rate) at a particular reproducible geometry can be determined by counting gamma standards, and a curve of peak counting efficiency vs. gamma energy for a particular detector obtained. Absolute gamma disintegration rates can be determined with a precision of about 5% from such a curve. Since for activation analysis a standard is commonly irradiated with the unknown, greater precision can usually be obtained. Lithium drifted germanium gamma detectors will easily resolve gamma rays that differ in energy by 5 or 10 keV and allow the intensities of each ray to be measured.

A lithium drifted germanium gamma spectrum of ^{56}Mn is shown in Figure V.4. The spectrum was taken with a 2 cm³ planar detector using a 1024 channel analyzer. It clearly shows the single escape (SE) and double escape (DE) peaks

FIGURE V.4

Ge(Li) GAMMA SPECTRUM OF ^{56}Mn



from the higher energy gamma rays. The spectrum can be compared with the NaI(Tl) spectrum shown in Figure V.3 which was taken on the same sample.

If Ge(Li) counters are used, the major gamma rays of ^{56}Mn can usually be seen without chemical separation on most neutron irradiated rocks and much biological material. A major interference is often sodium (15 hr. ^{24}Na) and a single precipitation of MnO_2 from a nitric acid solution plus KBrO_3 or KClO_3 will usually be adequate to remove Na and some other interferences. Lithium drifted germanium gamma spectra, because of the excellent energy resolution, lend themselves to computer processing and analysis of the data. Even though germanium detectors have very high resolution, it is essential to check that there are no interfering gamma rays, especially if computer data processing is being used. Thus if manganese is being determined on a new type of sample, it would be well to check by following the decay of the gamma peaks and by doing radiochemical separations to be sure there are no interferences.

Beta particle counting can also be used, especially for ^{56}Mn , and has the advantage that it requires a minimum of equipment. The most commonly encountered nuclide, ^{56}Mn , emits mainly energetic beta rays: 2.84 MeV (47%), 1.03 MeV (34%), and 0.72 MeV (18%). Two other nuclides, 45 min ^{51}Mn (emitting 2.17 MeV positrons 97% abundant) and 21 min ^{52}Mn (emitting 2.63 MeV positrons 92% abundant) emit high energy particles. These three nuclides could, therefore, be counted and sample self absorption corrections made fairly easily. The nuclide, 5.7 day ^{52}Mn decays about 2/3 of the time by electron capture but does emit positrons, 0.575 MeV (33%). Both 1.9×10^6 year ^{53}Mn and 303 day ^{54}Mn decay entirely by electron capture (^{54}Mn does have a 100% 835 keV gamma), but can be counted with fair efficiency with an argon beryllium window flow or G.M. counter. Self absorption corrections are very difficult to make for the weak 5.4 keV Cr K X-rays from manganese electron capture and also corrections need to be made for the ratio of K to L capture. Special equipment has been developed to count weak X-rays in the presence of a high energy gamma ray background⁽⁹⁴⁾. High resolution lithium drifted silicon photon counters with

beryllium windows are particularly valuable for counting low energy X-rays. Those manganese isotopes emitting both particles and gamma rays can be advantageously determined by $\beta\gamma$ beta-gamma coincidence counting⁽⁹⁵⁾.

The nuclide ^{56}Mn emits some high energy gamma rays, 2.110 MeV (15%), 2.520 MeV (1.2%), 2.950 MeV (0.4%), and 3.390 MeV (0.21%) which have sufficient energy to produce photoneutrons from beryllium and, except for the first, deuterium. The counting of photoneutrons produced in D_2O has been used to determine ^{56}Mn in activation analysis⁽⁹⁶⁾.

VI MANGANESE SEPARATION PROCEDURES

A number of methods have been used to separate and purify radioactive manganese for activation analysis, tracer production, reaction yield determinations, and analysis of radioactive contamination. Standardized manganese solutions to be used as carrier can be prepared by dissolving a known amount of manganese, either high purity electrolytic manganese metal or manganese sulfate ignited to 500°C , in dilute nitric acid and making up to volume. If the purified manganese from the radiochemical separation is MnO_2 , it is best to standardize the carrier by precipitation and weighing of MnO_2 since the dioxide is not quite stoichiometric and still contains a little water when dried at 110°C . Manganese carrier can also be standardized by titrimetric or colorimetric methods, see Section 3.

The methods that are included here have not necessarily been checked by the author. Procedure 1 is a general procedure which is fast and easy to carry out but which gives a relatively poor separation from a number of other elements. The additional steps in procedure 2 have been included to separate these contaminants. Procedure 3 is essentially procedure 1 applied for activation analysis. Procedures 4, 5, and 6 are brief outlines of some solvent extraction separations used for activation analysis. Procedures 7, 8, and 9 are taken from the previous edition of this monograph. Procedure 10 is the standard colorimetric analysis procedure for manganese and will be useful for

determining chemical yields.

Procedure 1

Introduction:

The precipitation of hydrated MnO_2 from a HNO_3 solution of Mn^{++} by oxidation with KBrO_3 or NaClO_3 is the most widely used separation method for manganese. It will separate manganese from most other elements; however, Si, W, Ta, Nb, and Pa are almost quantitatively carried and the precipitate will carry appreciable amounts of Fe, Zr, Ni, Co, V, and Sb. The precipitation is usually not quite quantitative. However, it is a very fast and useful step to concentrate manganese and separate it from most contaminants, and it will probably be the only step necessary if the activity is being counted with a lithium drifted germanium counter.

Source:

Step common to most procedures, see Leddicotte⁽⁹⁷⁾.

Material Analyzed:

^{51}Mn or ^{56}Mn for activation analysis or analysis of contamination.

Reagents:

Mn carrier, 10 mg/ml Mn as nitrate (Note 1.)

HNO_3 conc.

KBrO_3 solid

Hold back carriers, about 10 mg/ml

HNO_3 6N

H_2O_2 30%

Ethyl alcohol, 95%

Procedure:

Step 1. Dissolve sample in 6N to conc. HNO_3 (Note 2). Add about 20 mg Mn carrier. Add Fe(III) and Zr(IV) holdback carriers. Dilute to about 20 ml with 6N HNO_3 .

Step 2. Add about 100 mg solid KBrO_3 and heat to boiling. MnO_2 will precipitate and be coagulated by the heat. Cool. (Note 3).

Step 3. Centrifuge and discard supernate. Wash precipitate several times with 6N HNO_3 . Go to step 4 or 5 depending upon purity desired.

Step 4. Dissolve MnO_2 in 6N HNO_3 plus minimum H_2O_2 . Boil to destroy excess H_2O_2 . Repeat steps 1 through 3. Go to step 5 when sufficiently pure.

Step 5. Slurry MnO_2 with 0.1N HNO_3 and filter onto weighed filter paper disk about 2 cm diam. Use a Hirsch funnel or a sintered glass filtering apparatus. Wash precipitate with water and alcohol, dry at 100°C and weigh as MnO_2 .

Notes:

1. Standard Mn carrier can be made by dissolving an accurately weighed amount of 99.9% electrolytic Mn metal or MnSO_4 heated to 500°C in a little dilute HNO_3 and making up to volume. For best accuracy standardize as MnO_2 dried at 100°C .

2. Avoid excess chloride or sulfate since they tend to complex Mn and the chloride also reduces Mn(IV).

3. NaClO_3 can be used instead of KBrO_3 as the oxidant. It oxidizes the Mn more slowly but gives a more filterable precipitate.

Procedure 2

Introduction:

In this procedure for the separation of manganese from fission-product solutions, manganese is finally precipitated as $\text{MnNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ after standard decontamination steps. No detectable contamination was found in the manganese separated from 2.5×10^{11} fissions one hour old.

Source:

This procedure is taken from B. P. Bayhuret and R. J. Prestwood in the Collected Los Alamos Radiochemical Procedures⁽⁹⁸⁾.

Reagents:

Mn carrier, 10 mg/ml Mn as MnCl_2 in H_2O , standardized. (Note 1).

W carrier, 10 mg/ml W as $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ in H_2O .

Fe carrier, 10 mg/ml Fe as FeCl_3 in 1M HCl .

Pd carrier, 10 mg/ml Pd as $\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$ in 1M HCl.

Zr carrier, 10 mg/ml Zr as $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ in 1M HCl.

HCl, conc. and 6M.

HNO_3 , conc.

CH_3COOH glacial.

NH_4OH , conc.

NaOH, 10M.

H_2S gas.

NaBrO_3 , saturated solution.

$(\text{NH}_4)_2\text{S}$ 20% solution.

$(\text{NH}_4)_2\text{HPO}_4$, 1.5M.

Aerosol, 0.1% in H_2O .

Dowex AG 50-X4, 100-200 mesh cation resin.

Dowex AO 1-X8, 50-100 mesh anion resin.

Ethanol, absolute.

Procedure:

Step 1. Add the samples to 2 ml Mn carrier in a 40 ml conical centrifuge tube and adjust the volume to about 20 ml with conc. HNO_3 .

Step 2. Add 5 drops W carrier and heat on a steam bath for 5-10 min. Centrifuge, transfer the supernate to a clean centrifuge tube, and repeat the W scavenge.

Step 3. To the supernate from the second W scavenge add 3 ml satd. NaBrO_3 and heat on a steam bath. MnO_2 begins to precipitate and the solution fizzes. Carefully add another 3 ml NaBrO_3 and heat on steam bath for a total of about 10 min. Cool, add H_2O to fill tube, centrifuge. Discard supernate, wash precipitate twice with H_2O discarding washings.

Step 4. To the precipitate add 2 drops Fe carrier and 6 ml conc. HCl and boil down to a volume of about 3 ml. Dilute to 20 ml with H_2O , add conc. NH_4OH dropwise until $\text{Fe}(\text{OH})_3$ precipitates, and then 1-2 drops in excess. Heat on a steam bath for about 2 min and centrifuge. Transfer supernate to a clean

tube and repeat the Fe scavenge. Centrifuge and transfer second supernate to a clean tube.

Step 5. Add 2 ml of 20% $(\text{NH}_4)_2\text{S}$, heat for 1-2 min on a steam bath and centrifuge saving MnS precipitate.

Step 6. To the precipitate add 5 ml glacial CH_3COOH and boil over a flame. Add 5 drops Pd carrier, dilute to 20 ml with H_2O , place on a steam bath and bubble in H_2S . Centrifuge and save supernate in a clean tube. Repeat the scavenge with 5 more drops Pd carrier and again save supernate.

Step 7. To the supernate add 3 ml of 1.5M $(\text{NH}_4)_2\text{HPO}_4$ and about 5 drops conc HCl and boil. Add 2 drops Zr carrier, centrifuge, and save supernate. Repeat Zr scavenge and again save supernate.

Step 8. To the supernate add conc. NH_4OH dropwise until $\text{MnNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ precipitates and then heat on a steam bath for 3-5 min. Cool, centrifuge, and discard supernate. Wash precipitate with water.

Step 9. Dissolve the precipitate in 2-3 drops conc. HCl, dilute to 5-7 ml with H_2O , and place on a Dowex AG 50- H_4 , 100-200 mesh cation resin column (6 mm diam, 3 cm. long). Rinse tube with H_2O and add rinsings to column. Wash column with 2-3 ml portions of H_2O and discard washings. Place the cation column on top of an anion column (Dowex AG 1- B , 50-100 mesh, 8 mm diam, 4-5 cm long) and elute with 6-7 ml 6M HCl letting eluate from cation column drip through anion column. The Mn is in the eluate from the anion column. Collect the eluate in a clean centrifuge tube, add 10M NaOH dropwise to precipitate $\text{Mn}(\text{OH})_2$. Centrifuge.

Step 10. Dissolve the precipitate in 10 ml conc HNO_3 , boil solution until no color left, then repeat W scavenge, step 2.

Step 11. Repeat step 3.

Step 12. Repeat Fe scavenge, step 4.

Step 13. Repeat MnS precipitation, step 5.

Step 14. Repeat PdS scavenge, step 6.

Step 15. Repeat Zr phosphate scavenge, step 7.

Step 16. To the supernate add conc NH_4OH dropwise until $\text{MnNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ precipitates and then heat on a steam bath for 3-5 min. Centrifuge, discard supernats. Dissolve precipitate in 4-5 drops conc HCl . Dilute to 20 ml with H_2O , add a few drops arocoel and centrifuge. Save the supernats in a clean tube and reprecipitate $\text{MnNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ by adding $(\text{NH}_4)_2\text{HPO}_4$ then NH_4OH . Filter onto a weighed No. 42 Whatman 7/8" (about 2 cm.) filter circle using a ground off Hirsch funnel and a filter chimney. Wash the precipitate first with 0.1 M NH_4OH and then ethanol. Dry at 110°C , cool, weigh, and mount.

Notes:

Manganese carrier is made by dissolving 22.9 grams MnCl_2 in H_2O and diluting to 1 liter. To standardize, a 2.00 ml aliquot is pipeted into a 40 ml centrifuge tube, 5 drops conc HCl added, then 3 ml 1.5M $(\text{NH}_4)_2\text{HPO}_4$, then NH_4OH added to make the solution basic. The solution is heated to boiling, then let standing for 10 min. The precipitate is then filtered quantitatively into a weighed sintered glass crucible, washed with 0.1 M NH_4OH , then alcohol, then dried at 110°C and weighed as $\text{MnNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$.

Procedure 3

Introduction:

Even with fairly low power reactors, flux around $5 \times 10^{11} \text{ n/cm}^2 \text{ sec}$, manganese can be determined at the nanogram level. Manganese is determined by comparing the ^{56}Mn activity produced in the unknown with that produced in a dilute Mn in Al alloy comparator sample. Iron and cobalt can interfere due to the fast neutron reactions: $^{56}\text{Fe}(n,p)^{56}\text{Mn}$ and $^{59}\text{Co}(n,\alpha)^{56}\text{Mn}$. Since these reactions, unlike the $^{55}\text{Mn}(n,\gamma)^{56}\text{Mn}$ reaction, do not occur with thermal neutrons, the interference can be minimized by irradiating the samples in a highly thermalized flux. Also, the ^{56}Mn produced from iron and cobalt can be determined by irradiating the samples in a hard (large fast neutron component) flux and a highly thermalized flux.

Sources:

W. T. Mulline and G. W. Leddicotte, "Activation Analysis of Manganese -

Reactor Irradiation Source", Oak Ridge Master Analytical Manual, 5 11480⁽⁹⁹⁾.

Reagents:

NH_4OH 15N, stock 28% NH_3 .

Coagulant No. 78. Slurry 1 g of No. 78 ore flocculant vegetable colloid (Burtonite Company, Nutley, New Jersey) in 1 liter H_2O .

$(\text{C}_2\text{H}_5)_2\text{O}$, anhydrous.

Holdback carriers, about 10 mg/ml.

6N HCl, 500 ml conc. HCl per liter solution.

30% H_2O_2 .

Dilute (typically about 1.1%) Mn in Al alloy, spectrographically pure, comparator sample.

3M HNO_3 , 195 ml conc. HNO_3 per liter solution.

KClO_3 , solid.

Samples:

Unknowns, weigh out to better than 1%, 100 to 200 mg samples of solid or take to better than 1%, 5 to 25 ml samples of liquids. Comparator samples, weigh 25 to 30 mg samples to ± 0.1 mg.

Irradiation:

Irradiate samples in polyethylene or quartz ampoules. Irradiate for about 2.5 hours (less if ultimate sensitivity not needed).

Procedure:

A. Comparator samples: Transfer quantitatively to a 10 ml volumetric flask. Dissolve in minimum conc. HCl, dilute to volume, mix well (watch radiation dose). Take 1.00 ml aliquots in 50 ml centrifuge tubes, add 2.00 ml standardized Mn carrier plus about 1 ml each Cu^{++} , Ni^{++} , and Na^+ holdback carriers. Dilute to 20 ml with H_2O , mix, make alkaline with NH_4OH and continue as in part C.

B. Unknowns: If solid, transfer quantitatively to a 50 ml centrifuge tube, add 2.00 ml standardized Mn carrier and about 1 ml each Cu^{++} , Ni^{++} , and Na^+ holdback. Add sufficient mineral acid to dissolve sample, heating if necessary.

Dilute to 20 ml, make basic with NH_4OH , and continue as in part C. If liquid unknown, pipet a known aliquot into a 50 ml centrifuge tube, add 2.00 ml standardized Mn carrier and about 1 ml each Cu^{++} , Ni^{++} , and Na^+ holdback, dilute to 20 ml, make basic with NH_4OH , and continue as in part C.

C. Radiochemical separation:

Step 1. To NH_4OH solution add 5 drops 30% H_2O_2 , heat to boiling and centrifuge, saving the MnO_2 precipitate. Wash precipitate first with 20 ml 1M NH_4OH then with 20 ml 3M HNO_3 (Note 1).

Step 2. Dissolve MnO_2 in 2 ml 6N HCl and dilute to 10 ml with conc. HNO_3 . Heat and boil 30 sec. Add solid KClO_3 in 0.5 g increments, heating to 75°C after each addition (Note 2) until MnO_2 precipitation is complete. Centrifuge, wash MnO_2 precipitate with 25 ml 3M HNO_3 .

Step 3. Slurry MnO_2 with a little H_2O plus coagulant No. 76. Filter MnO_2 through a weighed filter paper circle held in a Hirsch funnel. Wash three times with 5 ml portions each of H_2O , 95% $\text{C}_2\text{H}_5\text{OH}$, then ethyl ether. Dry at 100°C and weigh to determine manganese yield, then mount for counting. The chemical yield should be well over 50%.

D. Counting:

The ^{56}Mn can be determined by either beta or gamma counting. Gamma counting with a scintillation spectrometer, or even better a lithium drifted germanium spectrometer, is preferable since the ^{56}Mn activity can usually be accurately determined in the presence of radioactive impurities. Since the manganese activity of the unknown is being measured against a known comparator sample, it is only necessary to mount and count the unknown and known samples in exactly the same way and to correct for decay and chemical yield.

Beta Counting:

Mount the unknown and known comparator samples in the same way, usually on a cardboard mounting card, covering them with a thin layer of cellophane or Scotch tape to contain the samples. Using a Geiger-Müller counter or a flow proportional counter determine the background and the counting rates (at the

same geometry and with the same added absorber) of the known and unknown. Correct the counts to the same decay time and for chemical yields and calculate the manganese content of the unknown. If the MnO_2 samples are of considerably different size, errors will be introduced because of sample self absorption and backscattering. Empirical corrections can be applied.

If the radiochemical purity of the unknown sample is questionable, follow the decay of the sample or take an aluminum absorption curve.

Gamma Countings:

Mount the unknown and known comparator samples in the same way and count at the same counter geometry and with the same added absorber. Use a scintillation spectrometer or a Ge(Li) spectrometer. Determine the peak counting rate of the 847 keV photopeak by integrating under the peak and subtracting off the extrapolated Compton background from the higher energy gamma rays. If the sample is radiochemically pure it is sufficient to integrate over the peak and subtract the counter background in the same channels. If there is an interfering impurity, integrate the 1811 or 2110 keV photopeaks. Correct for the difference in decay times and chemical yields and calculate the manganese in the unknown. It may be convenient to count the sample first (e.g. still in the centrifuge tube) and determine the manganese yield colorimetrically later.

Notes:

1. It is imperative that all the H_2O_2 be washed out before the MnO_2 is washed with 3M HNO_3 , otherwise it will dissolve.
2. KBrO_3 can be used instead of KClO_3 to precipitate MnO_2 . It reacts more rapidly but gives a less easily filterable precipitate. Step 2 of the procedure can be repeated for greater purity.

Procedure 4

Introduction:

Tetraphenylarsonium permanganate is extracted by CHCl_3 , relatively few other elements extract; it is therefore a good purification step for Mn. In this procedure a substoichiometric amount of tetraphenylarsonium chloride is

used so that the yields for the unknown and comparator samples will be essentially the same.

Sources:

A. Zeman, J. Prasilova and J. Ruzicka⁽¹⁰⁰⁾

Reagents:

1N and conc. H_2SO_4

Mn carrier, 1.6×10^{-2} M $MnSO_4$

H_3PO_4 , 85%

$AgNO_3$, 1% solution

$(NH_4)_2S_2O_8$

NH_4OH solution

tetraphenylarsonium chloride, 2×10^{-3} M

$CHCl_3$

Procedures:

Step 1. Irradiate unknown and comparator samples. Dissolve samples in 10 ml 1N H_2SO_4 (samples were chalk) (Note 1). Add 0.60 ml Mn carrier, 2 drops 85% H_3PO_4 , and dilute to 50 ml with water (Note 2). Now add 1 ml conc. H_2SO_4 , 1 ml 1% $AgNO_3$ and 1 g $(NH_4)_2S_2O_8$ and heat to oxidize manganese to MnO_4^- . Boil to destroy excess persulfate.

Step 2. Cool, adjust pH to 8-9 with NH_4OH (Note 3). Transfer to a separatory funnel, add 2.00 ml 2×10^{-3} M tetraphenylarsonium chloride then add 5.00 ml $CHCl_3$ and extract permanganate for 3 minutes (Note 4).

Step 3. Either measure activity in 3.00 ml of the $CHCl_3$ extract or evaporate to dryness and take up in 2 ml hot conc. HCl. Proceed in the same way with both known and unknown samples and assume yields the same for both.

Notes:

1. H_2SO_4 is the best acid for dissolution since SO_4^{2-} is not extracted. With HCl, Fe(III), Sn(IV), Pd(II), etc. can interfere. Nitrates extracts.

2. If Au, Re, or Tc are present, add a purification step by extracting manganese diethyldithiocarbamate complex. To the sample in H_2SO_4 with Mn

carrier added and pH adjusted to 8 add 5 to 10 fold excess Na diethyldithiocarbamate and extract precipitate with 10 ml CHCl_3 . The Mn(II) is air oxidized to Mn(III) and extracts as the Mn(III) complex^(100b).

3. At pH 8, MoO_4^{2-} and CrO_4^{2-} do not extract.

4. A substoichiometric amount of tetraphenylarsonium chloride is used. Manganese in the unknown is equal to the manganese in the comparator sample times the ratio of the activities in the unknown to the comparator sample (corrected for decay).

Procedure 5

Introduction:

This procedure was developed to separate and concentrate manganese prior to colorimetric analysis. It is based upon solvent extraction and could be adapted for activation analysis.

Source:

W. B. Healy, Anal. Chim. Acta. 34, 228, (1966)^(58a)

Reagents:

citric acid

NH_4OH , 6M, 1M

sodium diethyldithiocarbamate

CHCl_3

HCl , 3M

H_2SO_4

HNO_3

HClO_4

Procedure:

Step 1. Ash bone, teeth, milk, etc. unknowns. Irradiate with known comparator samples. Add 2 g citric acid per gram ash and dilute to about 175 ml.

Step 2. Adjust pH to about 5.2 by adding 6M NH_4OH using a glass electrode and a pH meter to monitor the pH. Add 0.4 g sodium diethyldithiocarbamate (DIECA). Adjust pH to 5.3 with 1 M NH_4OH and dilute to 200 ml.

Step 3. Extract with 25 ml CHCl_3 . Extraction causes pH to rise to about 5.8, readjust to 5.3 with about 1 ml 3 M HCl . About 90% of Mn in extract.

Step 4. Add 0.4 g more DIECA and reextract; about 90% of remaining Mn extracts. Ca phosphate only very slowly precipitates.

Step 5. Evaporate CHCl_3 extract, digest with H_2SO_4 - HNO_3 - HClO_4 . Count and determine Mn colorimetrically.

Procedure 6

Introduction:

TTA will complex Mn(II) at a fairly high pH. The extraction of the TTA complex has been used to purify manganese for activation analysis. The samples, if biological, are ashed and irradiated in a neutron flux of about 7.5×10^{12} n/cm² sec.

Source:

F. Kukula, B. Mudrova and M. Krivanek⁽⁵⁹⁾.

Reagents:

Mn carrier, MnSO_4 in H_2O , 1 mg/ml

Buffer, $\text{CH}_3\text{COONH}_4$ plus NH_4OH

sodium tartrate, 10%

KF, 20%

thenoyltrifluoroacetone (TTA) in ethanol, 0.11 M

TTA in ethyl acetate, 0.2 M

hydroxylamine hydrochloride

HCl

Procedure:

Step 1. Dissolve irradiated ash, etc., in HCl (use HNO_3 - HF for Zr-Al alloy). Add 2 ml Mn carrier, 3 ml 10% tartrate, 3 ml 20% KF (Note 1), 10 mg hydroxylamine hydrochloride, and adjust pH to 8 - 8.5 with the NH_4OH - $\text{CH}_3\text{COONH}_4$ buffer (Note 2). Add 0.5 ml TTA in ethanol (complexes about 70% of Mn).

Step 2. Extract 2 to 3 min with 10 ml TTA in ethyl acetate. Measure gamma spectrum of extract. Determine yields colorimetrically.

Notes:

1. Zr, Hf, Nb, Th, Fe, Sc, and Sb are prevented from extracting by the fluoride and tartrate, Cu and Co by the NH_4OH .
2. $\text{Mn}(\text{OH})_2$ does not precipitate at pH 8-8.5. Hydroxylamine hydrochloride is added to prevent the air oxidation of $\text{Mn}(\text{II})$.

Procedure 7

Introduction:

This procedure was developed for the neutron activation analysis of manganese in biological material (blood). It gives a manganese yield of 60 - 90% and takes about 2.5 hours for eight samples. The fraction of ^{24}Na left is about $5 \times 10^{-9}\%$ and ^{32}P , $2.2 \times 10^{-3}\%$.

Source:

H. J. Bowen⁽¹⁰¹⁾ as reported by Leddicotte⁽⁹⁷⁾.

Reagents:

fuming HNO_3
standardized Mn carrier
holdback carriers, about 10 mg/ml, of Br, Cl, Co, Cr, Cu, Fe, Ni, Na, K, Y, and Zn.
 H_2O_2 , 30%
 Na_2CO_3 solution
6M HCl
 $(\text{NH}_4)_2\text{HPO}_4$ solution
 $\text{CH}_3\text{COONH}_4$ solution
2M HNO_3
 NaBrO_3 solution, saturated
acetone

Procedures:

Step 1. Dissolve the irradiated blood in hot fuming nitric acid containing 50 mg manganese carrier and the holdback carriers listed under reagents. Precipitate manganese dioxide by adding NaClO_3 solution and heating. Centrifuge,

discard supernate.

Step 2. Wash MnO_2 twice with water, centrifuge and discard washes.

Step 3. Dissolve MnO_2 in acidified H_2O_2 , then precipitate MnCO_3 by adding Na_2CO_3 solution. Centrifuge, discard supernate.

Step 4. Wash precipitate with water. Dissolve precipitate in dil HCl and add FeCl_3 , ammonium phosphate, and ammonium acetate solutions. Precipitate $\text{Fe}(\text{OH})_3$ with NH_4OH . Centrifuge and save solution. Repeat scavenge by adding more Fe carrier, centrifuge, and save solution.

Step 5. To solution add enough Na_2CO_3 to precipitate MnCO_3 . Centrifuge and save precipitate.

Step 6. Dissolve the MnCO_3 in 2N HNO_3 and precipitate MnO_2 by adding saturated NaBrO_3 to the solution and heating. Centrifuge, save precipitate.

Step 7. Wash the MnO_2 three times with water and once with acetone. Centrifuge, discard washes. Transfer MnO_2 to a weighed counting tray, dry under an infrared lamp, and weigh to determine chemical yield.

Step 8. Cover tray with Scotch tape and beta or gamma count ^{56}Mn .

Procedure 8

Introduction:

This procedure was developed for the neutron activation analysis of manganese in biological materials (tomato seeds). It gives good decontamination from P and Na and takes about 2.5 hours. Chemical yield should be 60 - 90%.

Source:

H. J. M. Bowen and P. A. Caves⁽¹⁰²⁾ as reported by Leddicotte⁽⁹⁷⁾.

Reagents:

HNO_3 , conc.

standardised Mn carrier

Cu, Y, PO_4^{3-} holdback carriers, about 10 mg/ml.

NaClO_3 , saturated solution

2M HCl

30% H_2O_2

NH_4OH , conc.

$\text{CH}_3\text{COONH}_4$ solution

$\text{Fe}(\text{NO}_3)_3$ in dil HNO_3 about 10 mg/ml Fe

$\text{NH}_4\text{H}_2\text{PO}_4$

$\text{Cu}(\text{NO}_3)_2$, about 10 mg/ml Cu

ammonium sulfide solution

Procedure:

Step 1. Transfer the irradiated tissue from the irradiation container to a 50 ml centrifuge tube. Add 10 ml conc HNO_3 , 10 mg Mn carrier and holdback carrier of Cu, Y, and PO_4^{3-} . Boil the mixture until the tissue dissolves. Add 1 ml NaClO_3 , heat, centrifuge and save MnO_2 precipitate.

Step 2. Wash the MnO_2 twice with 5 ml H_2O . Centrifuge, discard wash. Dissolve MnO_2 in 3 ml 2N HCl and min. H_2O_2 and then add NH_4OH and $\text{CH}_3\text{COONH}_4$. Be sure all H_2O_2 is boiled out first. To this mixture add 5 drops of $\text{Fe}(\text{NO}_3)_3$ and one drop $\text{NH}_4\text{H}_2\text{PO}_4$. Centrifuge, discard precipitate.

Step 3. Acidify the supernate with 2N HCl , add 3 drops $\text{Cu}(\text{NO}_3)_2$ and enough NH_4HS to precipitate CuS . Centrifuge, saving supernate. Wash CuS once with 2N HCl and add wash to supernate.

Step 4. Make the solution alkaline with 3 ml NH_4HS and NH_4OH , boil, then centrifuge. Save MnS precipitate.

Step 5. Wash MnS twice with H_2O . Centrifuge. Dissolve MnS in 10 ml of conc HNO_3 and add 1 ml NaClO_3 . Boil (caution!), centrifuge and discard supernate.

Step 6. Wash the MnO_2 precipitate with three 10 ml portions of hot water. Discard washes.

Step 7. Slurry the MnO_2 precipitate with water into a weighed counting tray. Dry under an infrared lamp, cool, weigh to determine yield.

Step 8. Cover the tray with Scotch tape and beta or gamma count ⁵⁶Mn.

Procedure 9

Introduction:

This procedure was developed to determine manganese isotopes in cyclotron irradiated copper. The separation time is 30 min. and a decontamination of greater than 10^3 from other elements is reported. Chemical yield about 75%.

Source:

Batzel as reported by W. W. Meinke⁽¹⁰³⁾. Several other manganese procedures are given by Meinke. They are similar to this procedure except a different step is included to remove the target material.

Reagents:

HNO₃, conc.

Standardized Mn carrier

Holdback carriers, Zn, Ni, Co, Fe, Cr, V, Ti, Sc, Ca, and K. About 10 mg/μl

H₂S gas

HCl, 6M

NH₄OH, conc.

KClO₃ solid

H₂O₂, 30%

Procedure:

Step 1. Dissolve the copper in the minimum amount of conc HNO₃. Boil almost to dryness, add carriers, Zn and below, including 5 mg of standardized Mn. Make about 1M in HCl.

Step 2. Precipitate CuS by bubbling in H₂S. Centrifuge, leave supernate. Make supernate alkaline with NH₄OH and bubble in more H₂S to precipitate sulfides including MnS. Centrifuge and wash.

Step 3. Dissolve sulfides in 4 ml fuming HNO₃. Add 2 or 3 crystals of KClO₃ and boil gently for 2 minutes to precipitate MnO₂.

Step 4. Wash precipitate with H₂O, then dissolve in minimum HNO₃ and H₂O₂. Again add holdback carriers and make 16N in HNO₃. Heat and precipitate MnO₂ with KClO₃ as in step 3.

Step 5. Wash, filter, dry, weigh, and mount MnO_2 precipitate. Beta or gamma count.

Procedure 10

Introduction:

The manganese yield from a radiochemical separation can often be more conveniently determined by colorimetric analysis than by weighing. If the concentration of manganese is in the optimum region, a precision of 0.5% standard deviation can be obtained, considerably better than that obtained by weighing MnO_2 or $\text{MnNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$.

Source:

I. M. Kolthoff and P. J. Elving, "Treatise on Analytical Chemistry" (34).

Reagents:

6M HNO_3

H_2O_2 , 30%

H_2SO_4 , conc.

H_3PO_4 , 85%

KIO_4 , solid

Procedure:

Step 1. After counting is completed analyze the sample. If the sample is solid, dissolve it in 6M HNO_3 (plus a little H_2O_2 in the case of MnO_2) and make up to a convenient volume (10.0 ml) in a volumetric flask, and take an aliquot estimated to contain 0.5 to 1.0 mg Mn. If the sample is liquid, take a same sized aliquot.

Step 2. Add the aliquot to about 10 ml 6M HNO_3 , boil to remove H_2O_2 and oxidize Fe(II) and other reducing agents. If the solution contains much HCl, the aliquot should be added to conc. H_2SO_4 and the solution evaporated to fumes of SO_3 . Then, after the solution is cold, carefully add about 10 ml 6M HNO_3 .

Step 3. Dilute the solution to about 20 ml with H_2O and add about 5 ml 85% H_3PO_4 (decolorizes Fe(III)), then about 0.1 g KIO_4 . Heat to boiling and boil very gently for about 1 min., then add 0.1 g KIO_4 more and again boil

gently for 1 min.

Step 4. Cool solution, transfer to a 100 ml volumetric flask, make up to volume, take samples and determine the transmittance at 525 millimicrons using a spectrophotometer.

Step 5. Take a series of known manganese samples, oxidize, and establish a working curve. For a narrow band spectrophotometer, Beer's law holds.

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